INTERANNUAL VARIATIONS IN THE CARBON TO CHLOROPHYLL *a* RATIOS DURING THE SPRING BLOOM IN PRINCE WILLIAM SOUND, ALASKA

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A

THESIS

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ABSTRACT

The carbon to chlorophyll *a* ratio of phytoplankton during the spring bloom in Prince William Sound, Alaska was investigated for 3 seasons and related to major physical and chemical variables. Carbon to chlorophyll *a* ratios (C:Chl) were determined by two methods, based on particulate organic carbon to chlorophyll (POC:Chl) and phytoplankton cell carbon to chlorophyll (PCC:Chl). These ratios were compared to a more commonly used estimate, a fixed ratio of C:Chl, taken from literature, for the spring phytoplankton community. The hypothesis that the C:Chl ratios were significantly different between years was proven false. This research indicates that the C:Chl ratio is primarily determined by species composition of the phytoplankton community rather than external factors such as nutrients, temperature or salinity. In addition, this research indicates that the identification and enumeration method, although rarely used because it is the most time and labor intensive method, provides the best estimate of phytoplankton carbon. The mean PCC:Chl ratio for all three years was 18, and is the best fixed ratio to estimate spring phytoplankton carbon in Prince William Sound when an El Niño is not present.

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INTRODUCTION

How much phytoplankton carbon is in a sample of water? Determining this apparently simple yet vital quantity accurately is far from straightforward. Researchers routinely determine a water sample's temperature, salinity, nutrients and chlorophyll; they describe ocean currents, undercurrents, eddies, and tides equally routinely. On the other hand, they find getting a direct and accurate measure of phytoplankton carbon to be a major challenge.

One difficulty in directly measuring phytoplankton carbon comes from the inability to separate phytoplankton carbon from that of detritus and heterotrophic microplankton (Banse 1977, Cullen 1982). Determining this important variable in biogeochemical models and food webs has been left to biomass indicators or experimental manipulations. Usually chlorophyll *a* (chlorophyll), a photosynthetic pigment, is used as an indicator of phytoplankton biomass. In this determination, chlorophyll is used as a proxy for carbon concentration by assuming a fixed carbon to chlorophyll ratio chosen from published literature and sometimes with consideration as to the type of nutrient regime being studied (Riemann et al 1989). Such ratios can range from 10 to 250 (see review by Cullen 1982). Due to the ease of estimating chlorophyll concentration (Zonneveld 1998), it is the most widely used index of phytoplankton biomass (Geider et al. 1997). The problem with using this conversion method is that the relationship of phytoplankton carbon to chlorophyll is not constant (Chang et al. 2003). Cellular chlorophyll and carbon concentrations vary due to physiology, species composition, and environmental conditions. These variations make the technique of using

a single and constant conversion factor highly controversial. Furthermore, some researchers have proposed (e.g., Cullen 1982) that chlorophyll distributions can vary independent of phytoplankton biomass.

The use of a fixed carbon to chlorophyll ratio (C:Chl) as an indicator of phytoplankton physiological condition and growth rate is widely applied (Cloern et al. 1995, Geider et al. 1997). On a cellular level, this ratio indicates the physiological status of the phytoplankton because it quantifies the amount of photosynthetic, light-absorbing resources allocated by a cell relative to its overall organic carbon content (Falkowski and Raven 1997).

In addition to using a fixed literature-based value to estimate the ratio, it can be estimated by two other methods commonly used to obtain a more accurate C:Chl ratio. One method compares subsamples of chlorophyll concentration, measured directly by fluorescence, to phytoplankton carbon, calculated by microscopic enumeration and cell measurement and then converted to biomass using equations based on cell volume. This method is considered to be the most reliable for estimating the ratio; it has the added ability to resolve species composition as well (Montagnes and Berges 1994, Smayda 1978, Eppley et al. 1977), but it is rarely used because it is time consuming and labor intensive (Redalje and Laws 1981, and Montagnes and Berges 1994). A second method is based on the linear regression of directly measured total particulate organic carbon in a water sample to the chlorophyll concentration of that sample. An error associated with this method is that the sample of particulate organic carbon can contain a large amount of non-phytoplankton carbon (Redalje and Laws 1981). Geider (1987) states that this

method can result in C:Chl values ranging from 20 to 300. Concerns regarding the limitations of this method have been expressed by Banse (1977), Andersson and Rudehäll (1993), and Geider et al. (1997).

Because the C:Chl ratio is a parameter vital to understanding and modeling ecosystem dynamics, a study comparing two years of data for this ratio from a single station in Prince William Sound, Alaska, became a part of the multidisciplinary SEA project (Ward 1997). Results from this study indicated that this ratio had varied approximately by a factor of two. This project is an extension of Ward's, utilizing an additional year of field work and a detailed examination of the ratio and its variability during the spring bloom for three years. The general hypothesis is that there are significant interannual differences in the C:Chl ratio during the spring bloom at this location. This hypothesis was tested by examining six parameters: cell numbers, cell size, cell volume, calculated carbon, direct measures of particulate organic carbon, and chlorophyll. C:Chl ratios were determined by three methods and related changes in the ratio to major physical and chemical variables.

Background: What Factors Determine the C:Chl Ratio in a Cell?

Variations in C:Chl have been suggested to be a function of cell size, light, nutrients, temperature and several other variables by many studies over the past 45 years. A brief review of the literature regarding the relationships of these environmental variables and C:Chl follows. A complete detailed review of these relationships, which is beyond the scope of this paper, can be found in the following articles: Tillman (1982),

Richardson et al. (1983), Falkowski et. al. (1985), Geider (1987), Raven and Geider (1988), Geider et al. (1997).

What is the Effect of Phytoplankton Cell Size and Chemical Composition on C:Chl?

Work by Taguchi (1976), Blasco et al. (1982), and Geider et al. (1986) suggests that cellular C:Chl ratios are independent of cell size and that variances in phytoplankton C:Chl ratios can be driven by differences in chemical composition of taxonomic groups. Work by both Hitchcock (1982) and Chan (1978) describes differences in the chemical composition of dinoflagellates and diatoms. Hitchcock states that the logs of cellular chlorophyll, carbohydrate, and lipid concentrations are directly related to the log of cell volume in both groups, but diatoms, in general, had lower concentrations than did dinoflagellates of equal sizes. Studies by Strathman (1967) indicate that diatoms contain less carbon per unit volume than do phytoflagellates. Strathman attributed this dissimilarity to the siliceous cell wall and significant vacuole volume in diatoms (Verity et al. 1992). As a general rule, the C:Chl ratio decreases from dinoflagellates to diatoms to chlorophytes, respectively (Geider et al. 1986, Chan 1978).

What is the Effect of Temperature on C:Chl?

Thompson et al. (1992) studied eight species of phytoplankton and found no increase in the amount of carbohydrate per cell with changes in temperature. However, their work did support previous studies showing a negative correlation between C:Chl and temperature (Geider 1987). Although most of the research involving phytoplankton physiological responses to changing temperature has been conducted on cultures, a few studies of natural populations support the idea that community C:Chl increases with

decreasing temperatures (reviewed in Geider 1987). The acclimation responses of phytoplankton to changing temperature most commonly seen at the biochemical level involve changes in enzymes, membrane composition, and the photosynthetic light-harvesting apparatus, which includes chlorophyll (Smith et al. 1994). Decreasing temperatures reduce the concentration of cellular chlorophyll resulting in an increase in membrane lipid/protein ratio (Raven and Geider 1988). This increased lipid/protein ratio is required at low temperatures to allow for continual fluidity of the thylakoid membrane. In addition, an increase in the ratio of lipid to protein in the thylakoid membrane may allow for adjustments of intermolecular forces between membrane components (Raison et al. 1980). These physiological changes observed in response to decreasing temperatures result in increasing C:Chl.

What is the Effect of Nutrient Concentrations on C:Chl?

Once a major nutrient concentration drops below that required to support the current uptake and growth rate, the general trend is for the algae cell to decrease its growth rate and the intracellular concentration of the limiting nutrient (i.e., the cell quota) so that it can continue to grow with the limited nutrient concentration available (Darley 1982). With increased limitation, a decrease in cellular chlorophyll and protein concentrations and an increase in the carbohydrate, and sometimes lipid concentrations, usually occur. In addition, physiological processes such as photosynthesis and respiration decline as well, so that the cell can utilize energy for synthesizing new uptake sites for the limiting nutrient (Darley 1982). During nutrient limitation, the cell quotas of carbon

and chlorophyll decrease concurrently, but chlorophyll decreases faster than carbon causing an increase in C:Chl.

What is the Effect of Light on C:Chl?

In nature, phytoplankton experience fluctuations in light intensity in response to physical dynamics such as cloud cover, vertical mixing and suspended particle concentration. Although different algal classes have different light requirements for growth and photosynthesis (Geider 1993, Richardson et al. 1983), the time a phytoplankton cell spends in its optimum light intensity environment is limited and each cell must adapt to irradiance extremes. The basic goal for a phytoplankton cell is to acquire the amount of light energy needed to maximize the cell's photosynthetic ability which in turn will maximize the growth rate. One way that phytoplankton can optimize their ability to harvest available light is to change the intracellular pigment content (Falkowski and Owens 1980). Too much light can damage the cell's photosynthetic apparatus and too little light slows photosynthesis. Both conditions have the ability to decrease the cell's growth rate. In cases of shade adaptation, phytoplankton can commit more of their resources to chlorophyll synthesis and photosynthesis than to the synthesis of ribulose bisphosphate carboxylase or other enzymes beneficial to cell growth (Darley 1982).

Falkowski and Owens (1980) described two types of adaptation for low-light environments, both of which increase the intracellular chlorophyll concentration. They found that the diatom *Skeletonema costatum* increased the *size* of its P700 photosynthetic units under low light. A photosynthetic unit is composed of photochemical reaction

centers that are coupled to antennae, which in turn harvest light energy and transfer it to reaction centers (Falkowski and Raven 1997). In contrast, a chlorophyte, *Dunaliella tertiolecta,* increased its cellular chlorophyll content under low light conditions by changing the *number* of P700 photosynthetic units, *not* the *size* of the units. Ultimately there is an increase in the intracellular chlorophyll concentration by either process, which results in a decrease in C:Chl. In contrast, in cases of too much light, cell growth is limited by the rate at which carbon is fixed (Darley 1982, Geider et al. 1997). Light-adapted cells have an increased C:Chl ratio because they utilize fewer resources to produce chlorophyll; instead, they utilize resources in other, non-photosynthetic cell functions (Falkowski and Raven 1997).

Summary

In marine phytoplankton, C:Chl is maximal at high light levels, low temperatures and under nutrient-limiting conditions. It is minimal at high temperatures, low irradiances and under nutrient-replete conditions (Geider et al. 1997 and Taylor et al. 1997).

METHODS

The Sound Ecosystem Assessment (SEA) Project was initiated in response to the *Exxon Valdez* oil spill that occurred during the spring of 1989 in Prince William Sound (PWS), Alaska. The main goal of SEA was to determine how the extensive oil spill affected biological conditions in Prince William Sound; specifically, the aim of the project was to develop ecosystem models relevant to the restoration of populations of pink salmon and herring. Understanding the controls of ecosystem processes that nourish the food web at its primary level is crucial to SEA's main goal (McRoy et al. 1998). This study takes an in-depth look into Ward's (1997) suggestion that there were interannual differences in the phytoplankton community C:Chl ratios from PWS in 1995 and 1996. The study is an extension of the Phytoplankton and Nutrient Component of SEA and was sponsored in part by a grant from the *Exxon Valdez* Oil Spill Trustee Council.

Study Area

Prince William Sound occupies some 8880 km^2 of the south-central coast of Alaska, forming a fjord-rimmed water body separated from the open Gulf of Alaska (GOA) by Montague and Hinchinbrook Islands. The sound is deep; the central basin ranges from 400 to 450 m and a smaller basin in the northwest reaches depths greater than 800 m (Vaughan et al. 2001). The sound is bound to the east, north, and west by the Chugach Mountains. Air masses from the GOA are uplifted over the mountains, producing frequent storms that release large amounts of rainfall into the sound (4-5 m of rain per year) (Cooney et al. 2001). In addition, the precipitation creates ice fields in the

mountains with alpine and tidewater glaciers that are sources of freshwater to the sound (Gay and Vaughan 2001).

Montague and Hinchinbrook, both large mountainous islands, separate the sound from the GOA (Figure 1). Hinchinbrook Entrance and Montague Strait are the two major passages connecting the sound to the GOA. In autumn and winter, strong onshore Ekman transport and coastal downwelling results in an upper layer transport into the Sound through Hinchinbrook Entrance and an outflow through Montague Strait (Niebauer et al. 1994, Gay and Vaughan 2001). Due to complicating factors such as stratification and an increased Alaska Current flow, both inflow and outflow have been observed at Hinchinbrook Entrance and Montague Strait during the summer and early autumn (Niebauer et al. 1994, Gay and Vaughan 2001). From autumn through spring strong southeast geostrophic winds over the northern GOA force onshore Ekman transport and coastal downwelling. A detailed description of PWS physical dynamics can be found in Niebauer et al. (1994).

Sampling

Work was conducted in Port San Juan using the Armin F. Koernig Hatchery (AFK) as a logistic and laboratory base. Water and biological samples were collected daily from a small skiff at a single station during the spring. The sampling station was located in the middle of Elrington Passage (60°01° 'N, 148°00° 'W) which had a bottom depth of 140 m (Figure 1). Sampling periods ranged from 60 - 77 days for each of the three years (1995, 1996 and 1997), beginning in early April and ending in mid-June. Temperature, salinity, and secchi depths were measured *in situ*. Water samples for

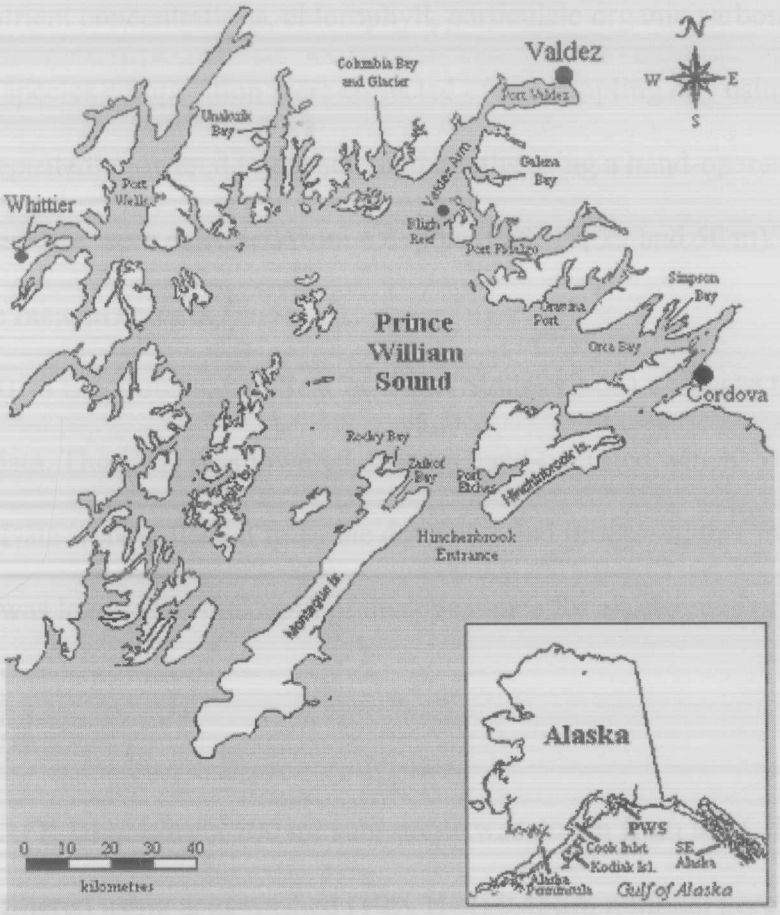

Figure 1. Map of Prince William Sound, Alaska showing Elrington Passage.

determining nutrient concentrations, chlorophyll, particulate organic carbon and phytoplankton species composition were collected every sampling day using a 5-liter Niskin bottle repeatedly lowered to the standard depths using a hand-operated winch. Whole water samples were collected from 6 depths (0, 5, 10, 25 and 50 m).

Hydrographic measurements

A Sea-Bird Electronics, Inc. SeaCat CTD (Model 19-03) was used to measure hydrographic data. The CTD was lowered, using a hand-operated winch, to 80 m each sampling day. Data were collected from the downcast and processed to 1 meter averages. A Secchi disk was lowered to the depth of disappearance for an estimate of water transparency.

Nutrients

At the AFK laboratory a 100 ml subsample was drawn from the 5-liter whole water sample, filtered using acid-washed (10% HCl) 0.45μm nominal pore size glass fiber filters, and stored frozen in acid-washed polypropylene bottles. Samples were processed at the University of Alaska laboratories in Fairbanks within 3-6 months after collection and analyzed for nitrate+nitrite (N+N), silicate (SiO_4), and phosphate (PO_4). Chemical analysis was performed using prescribed Continuous Flow Analysis techniques (Alpkem Corp. 1986) on an Alpken 305 auto analyzer (McRoy et al. 1999).

Chlorophyll *a*

At the AFK laboratory, a subsample (250-1000 ml) of sea water, from the 5-liter whole water, was filtered through 0.45 μm nominal pore size glass fiber filters (McRoy et al. 1999). Filters were ground, pigments were extracted in 10 ml of 90% acetone and

centrifuged for 10 minutes. After centrifuging, the fluorescence of the supernatant was then measured with a Turner Designs fluorometer, model 10-AU. The samples were corrected for phaeophytin concentration by adding three drops of 1N HCl to the sample, after which the fluorescence was again recorded. At the beginning of each field season, the fluorometer was calibrated against chlorophyll extracted from spinach, on a Hitachi spectrophotometer, model 100-40, using standard techniques outlined by Parsons et al. (1984).

Particulate Organic Carbon (POC)

A 1 liter water subsample from each depth was filtered onto a baked, 0.45 μm pore size, glass fiber filter and stored frozen in the dark in glass vials (McRoy et al. 1999). The samples were analyzed at the University of Alaska Fairbanks Stable Isotope Facility on a Europa 20-20 stable isotope mass spectrometer equipped with a C and N elemental analyzer. Before analysis, inorganic carbon was removed from the filters by fuming with 6N HCL in a desiccator for 4 hours. The laboratory standard was peptone and was referenced to Vienna Pee Dee Belemnite.

Cell Numbers and Community Composition

Water subsamples (50 ml) were filtered through a 220 μm mesh net to remove zooplankton and other large particles. Filtered samples were preserved at the AFK laboratory with Lugol's Solution and stored in plastic vials in the dark until analysis (within 6 months). At our UAF laboratory, a subset of samples from each year was selected based on the time series of chlorophyll concentrations to best describe the changes in phytoplankton during the bloom and post-bloom. A portion (25 ml) of each

preserved sample was settled in the dark for 24 hours and then analyzed for phytoplankton taxa identification and cell number using a Zeiss Televal 31inverted microscope (Utermohl 1931). Cells > 15 μm, observed in a rectangular field using 200 X magnification, were identified and counted until a minimum of 300 cells were totaled. Cells ≤15 μm were counted at 400 X across the same transects until a minimum of 300 cells were enumerated. The numbers of fields analyzed was recorded for abundance calculations.

Diatoms and small cells were identified using a compilation of taxonomic guides (Cupp 1943, Yamaji 1986, and Tomas 1996). In most cases diatoms were identified to at least genus and nanoplankton (2-20 μm) was identified to genus or class.

Phytoplankton Cell Carbon (PCC)

The methods used to calculate phytoplankton cell volume and estimate cell carbon (PCC) were initially established by Ward (1997) for the 1995 and 1996 sample series and extended to the 1997 samples. Average cell dimensions from the most abundant taxa were used to estimate phytoplankton biomass. Cell dimensions were calculated from measurements of length, width and depth. The length and width measurements (to the nearest 1 μm) were taken from 20 cells of each taxon and cell depth measurements were estimated from equations specific for each cell type.

Cell volumes (CV) were calculated using modified geometric shapes and volume equations from Kovala and Larrance (1966); see Table 1. From the calculated cell volumes, the PCC of the major taxa in a sample was estimated using two equations,

Table 1. Volume equations, cell measurements, cell volumes and cell carbon estimates for the most abundant taxa from Ward (1997).

Taxa	Voume Equation	Mean Diameter (μm) A	Mean Height (μm) B or C	Thickness (μm) B or C	Cell Volume (μm^3)	Carbon ($pg\ cell^{-1}$)
Chaetoceros sp. <25 μm	$V = BC(A-B+\pi/4(B))$	4.6	9.9	3.08	120.21	14.28
Chaetoceros sp. 25-44 μm	$V = BC(A-B+\pi/4(B))$	10.25	25.25	6.83	1514.9	97.44
Chaetoceros deciprens	$V = BC(A-B+\pi/4(B))$	24.65	19.9	13.27	5576.71	261.67
Flagilariopsis spp.	$V = ABC$	14.25	2.43	4.86	112.8	13.6
Leptocylindrus danicus	$V = ABC$	47.35	11.5	5.75	3131.02	168.94
Leptocylindrus minimus	$V = ABC$	26.75	2.75	1.38	101.15	12.52
Pseudo-Nitzschia sp. 25-44 μm	$V = \pi/6(ABC)$	33.9	2.15	1.07	41.36	6.36
Pseudo-Nitzschia sp. 45 μm	$V = \pi/6(ABC)$	52.3	2.5	1.25	85.6	11.04
Rhizosollenia fragilissima	$V = \pi/4(A^2B)$	22.4	5		1970.41	118.93
Skeletonema costatum	$V = \pi/4(A^2B)$	12.88	4.15		540.72	44.63
Thalassiosira sp. <25μm	$V = \pi/4(A^2B)$	18.88	10.35		2897.57	159.3
Thalassiosira sp. 25-44 μm	$V = \pi/4(A^2B)$	29.25	10.5		7055.55	312.74
Thalassiosira sp. >45μm	$V = \pi/4(A^2B)$	48.83	14.9		27902.92	886.75
Unidentified flagellates <10 μm	$V = \pi/4(A^3)$	5.75			99.54	18.63
Unidentified flagellates >10 μm	$V = \pi/4(A^3)$	13.44			1269.7	168.97

Note: Shapes and equations were modified from Kovala and Larrance (1966); carbon was calculated from Strathman's (1967) equations.

one for diatoms and another for all other species (Strathmann 1967):

Diatoms: log carbon = -0.422 + 0.758 (log CV)

Other Cells: log carbon = -0.460 + 0.866 (log CV)

where CV = cell volume.

The calculated cell volumes and carbon concentrations for the most abundant taxa were the same for all years.

The number of cells per milliliter was calculated from the following equation:

$$\frac{(\text{plate area/transect area}) * \text{number of species counted}}{\text{volume of sample settled}}$$

where (plate area/transect area) at 20 X = 39.53

(plate area/transect area) at 40 X =64.56

The PCC per milliliter (pg C ml^{-1}) was determined for each taxon by multiplying the amount of carbon in each cell by the number of cells per ml. The amount of carbon per sample was then converted from pg C ml^{-1} to mg C m^{-3} (or μg C l^{-1}).

Carbon to Chlorophyll *a* Ratios

Phytoplankton cell carbon to chlorophyll ratios (PCC:Chl) were determined by dividing the total amount of PCC in each subsample by the total measured amount of chlorophyll. Total particulate organic carbon to chlorophyll ratios (POC:Chl) were obtained by dividing the concentration of POC, obtained from direct measurements of a filtered water subsample, by the measured chlorophyll content of the water subsample.

RESULTS

Data were collected in Prince William Sound on 64, 73, and 77 consecutive days in the spring of 1995, 1996, and 1997, respectively (Table 2). Using chlorophyll as a guide, the spring cycle is divided into three periods: the bloom (which includes the initial rise), the seasonal maximum and decline of chlorophyll. The post-bloom, characterized as a period of low, relatively constant chlorophyll, and the recovery, a small increase in chlorophyll was observed following the bloom in early summer. This designation follows the convention developed by Ward (1997) who first described the spring bloom cycle in this location.

Table 2. Summary of measurements (by number) in Elrington Passage (60°01° 'N,148°00° 'W), Prince William Sound, Alaska.

Parameters	1995	1996	1997
Sampling Period (Julian Days)	107 - 170	97 - 169	90 - 166
Total Sampling Days	64	73	77
CTD Casts	63	73	63
Secchi Depth Measurements	63	73	73
Chlorophyll *a* Measurements	372	437	444
Nitrate+Nitrite Measurements	372	438	450
Silicate Measurements	369	438	450
Phosphate Measurements	372	438	450
Species Composition Determinations	54	64	51
Particulate Organic Carbon Measurements	300	380	277

The data describe the amount and composition of the spring phytoplankton increase and subsequent decline for each year in relation to selected environmental variables. Descriptive statistics for measured parameters can be found in Table 3.

Table 3. Summary of descriptive statistics for sample parameters for each year.

Parameter		Sample Depth	1995	1996	1997
Temperature (°C)		5 m			
	Mean ± (SE)		6.19 ± 0.18	6.01 ± 0.20	5.92 ± 0.20
	Minimum		4.13	3.90	3.74
	Maximum		9.07	9.97	10.11
	n		63	72	71
Salinity (psu)		5 m			
	Mean ± (SE)		30.01 ± 0.16	31.38 ± 0.05	31.10 ± 0.06
	Minimum		26.52	29.94	29.60
	Maximum		31.55	32.13	31.64
	n		63	72	71
N+N (µM)		5 m			
	Mean ± (SE)		4.76 ± 0.33	5.73 ± 0.30	3.16 ± 0.23
	Minimum		0.00	0.83	0.24
	Maximum		12.27	11.72	9.22
	n		62	73	73
Silicate (µM)		5 m			
	Mean ± (SE)		8.94 ± 0.49	9.69 ± 0.39	10.42 ± 0.66
	Minimum		0.37	2.24	0.88
	Maximum		19.75	18.15	21.64
	n		62	73	73
Phosphate (µM)		5 m			
	Mean ± (SE)		0.81 ± 0.04	0.83 ± 0.03	0.89 ± 0.04
	Minimum		0.24	0.39	0.17
	Maximum		1.78	1.37	1.72
	n		62	73	73
Secchi Depth (m)					
	Mean ± (SE)		7.06 ± 0.18	7.32 ± 0.32	7.06 ± 0.25
	Minimum		4.00	3.00	3.00
	Maximum		11.50	13.00	13.00
	n		63	73	62
Chlorophyll (µg l^{-1})		0-25 m			
	Mean ± (SE)		5.08 ± 0.35	6.64 ± 0.34	4.20 ± 1.04
	Minimum		0.56	0.26	0.76
	Maximum		18.85	19.84	13.48
	n		199	253	295

Table 3 cont. Summary of descriptive statistics for sample parameters for each year.

Parameter	Sample Depth	1995	1996	1997
Particulate Organic Carbon (POC) ($\mu g\ l^{-1}$)	0-25 m			
Mean ± (SE)		317.42 ± 10.03	352 .18 ± 10.07	251.29 ± 7.40
Minimum		104.23	109.00	91.60
Maximum		1028.25	1150.00	612.80
n		199	252	180
Phytoplankton Cell Carbon (PCC) ($\mu g\ l^{-1}$)	0-25 m			
Mean ± (SE)		120.86 ± 10.82	216.89 ± 20.62	106.76 ± 11.32
Minimum		8.42	11.90	13.70
Maximum		313.37	646.79	339.19
n		54	64	51
Depth Averaged Particulate Organic Carbon (POC_D)	0-25 m			
Mean ± (SE)		343.95 ± 15.22	342.87 ± 17.02	248.00 ± 12.62
Minimum		174.35	130.93	118.00
Maximum		609.99	722.67	537.43
n		51	64	49
Depth Averaged Phytoplankton Cell Carbon (PCC_D)	0-25 m			
Mean ± (SE)		117.39 ± 20.19	222.44 ± 41.48	110.21 ± 19.50
Minimum		16.26	15.64	24.90
Maximum		226.23	476.99	272.15
n		14	16	13

A complete list of all statistical comparisons of seasonal means is given in Table 4 and unless less stated otherwise all tests were conducted at $\alpha = 0.05$ significance level.

Hydrography

Temperature

CTD casts were done routinely each day from surface to near bottom. For purposes of this analysis the temperature and salinity data from 5 m are used to characterize the major differences in surface layer hydrography of each sampling year. The seasonal development of the euphotic zone temperature was strongly dependent on solar heating and progressed linearly as the spring developed (Figure 2). In 1995, the temperature increase was gradual; the minimum water temperature was 4.13 °C on day 108 and it reached a maximum of 9.07 °C during the recovery on day 166 (Figure 3).

In 1996 the water temperature gradually increased until day 152, after this date the water temperature sharply increased peaking at 9.85 °C on day 157. The temperature for 1996 showed one more abrupt increase on day 161 when it reached 9.97 °C. Temperatures in 1996 ranged from 3.90 to 9.97 °C.

The amount of variation in temperature due to time progression is slightly lower in 1997 ($r^2 = 0.83$) than in the previous two years. In 1997 temperatures gradually increased from the beginning of the sampling season until the post-bloom at which time the temperature increased from 5.92 °C on day 142 to 10.10 °C on day 148. The water temperature quickly dropped back down to 6.46 °C until day 158 when it began to increase again, reaching a maximum of 10.01 °C during the recovery. During the 1997 sampling season temperatures ranged from 3.74 - 10.10 °C.

Table 4. Results of Two Sample T-Test (t) or Two Sample Z-Test (z) comparing seasonal means of all parameters for study years.

Test	Parameter	Sample Depths	X_1	X_2	t or z	p value	
Z	Temperature (°C)	5 m	95	96	0.67	0.50	
			95	97	1.00	0.32	
			96	97	0.31	0.76	
Z	Salinity (psu)	5 m	95	96	8.02	0.00	*
			95	97	6.20	0.00	*
			96	97	3.64	0.00	*
Z	N+N (μM)	5 m	95	96	2.18	0.03	*
			95	97	3.95	0.00	*
			96	97	6.78	0.00	*
Z	Silicate (μM)	5 m	95	96	1.21	0.23	
			95	97	1.80	0.07	
			96	97	0.95	0.34	
Z	Phosphate (μM)	5 m	95	96	0.38	0.70	
			95	97	1.49	0.14	
			96	97	1.37	0.18	
Z	Chlorophyll ($\mu g\ l^{-1}$)	0-25 m	95	96	3.15	0.00	
			95	97	2.33	0.02	
			96	97	6.57	0.00	*
Z	Particulate Organic Carbon (POC) ($\mu g\ l^{-1}$)	0-25 m	95	96	2.45	0.01	*
			95	97	5.31	0.00	*
			96	97	8.07	0.00	*
Z	Phytoplankton Cell Carbon (PCC) ($\mu g\ l^{-1}$)	0-25 m	95	96	4.12	0.00	*
			95	97	0.78	0.44	
			96	97	4.68	0.00	*
Z	Particulate Organic Carbon Depth Averaged (POC_D)	0-25 m	95	96	0.05	0.48	
			95	97	4.85	0.00	*
			96	97	4.48	0.00	*

Table 4 cont. Results of Two Sample T-Test (t) or Two Sample Z-Test (z) comparing seasonal means of all parameters for study years.

Test	Parameter	Sample Depths	X_1	X_2	t or z	p value	
T	Phytoplankton Cell Carbon Depth Averaged (PCC_D)	0-25 m	95	96	2.28	0.02	*
			95	97	0.26	0.80	
			96	97	2.45	0.01	*
Z	Particulate Organic Carbon to Chlorophyll (POC_D:Chl_D)	0-25 m	95	96	2.12	0.03	*
			95	97	6.01	0.00	*
			96	97	4.28	0.00	*
T	Phytoplankton Cell Carbon to Chlorophyll (PCC_D:Chl_D)	0-25 m	95	96	5.31	0.00	*
			95	97	2.62	0.01	*
			96	97	2.03	0.04	*
Z	Cell Volume (μm^3 $cell^{-1}$)	0-25 m	95	96	6.53	0.00	*
			95	97	6.45	0.00	*
			96	97	8.97	0.00	*
Z	Cell Abundance (cells ml^{-1})	0-25 m	95	96	6.70	0.00	*
			95	97	7.27	0.00	*
			96	97	8.98	0.00	*
Z	Diatom Abundance (%)	0-25 m	95	96	6.84	0.00	*
			95	97	9.29	0.00	*
			96	97	1.26	0.21	
Z	Cellular Phytoplankton Carbon (pg $cell^{-1}$)	0-25 m	95	96	7.29	0.00	*
			95	97	6.94	0.00	*
			96	97	9.81	0.00	*
Z	Cellular Phytoplankton Chlorophyll (pg $cell^{-1}$)	0-25 m	95	96	7.69	0.00	*
			95	97	4.60	0.00	*
			96	97	9.27	0.00	*

* = $z_{.05}$ & $t_{.05}$ greater than the critical two-tail 1.96

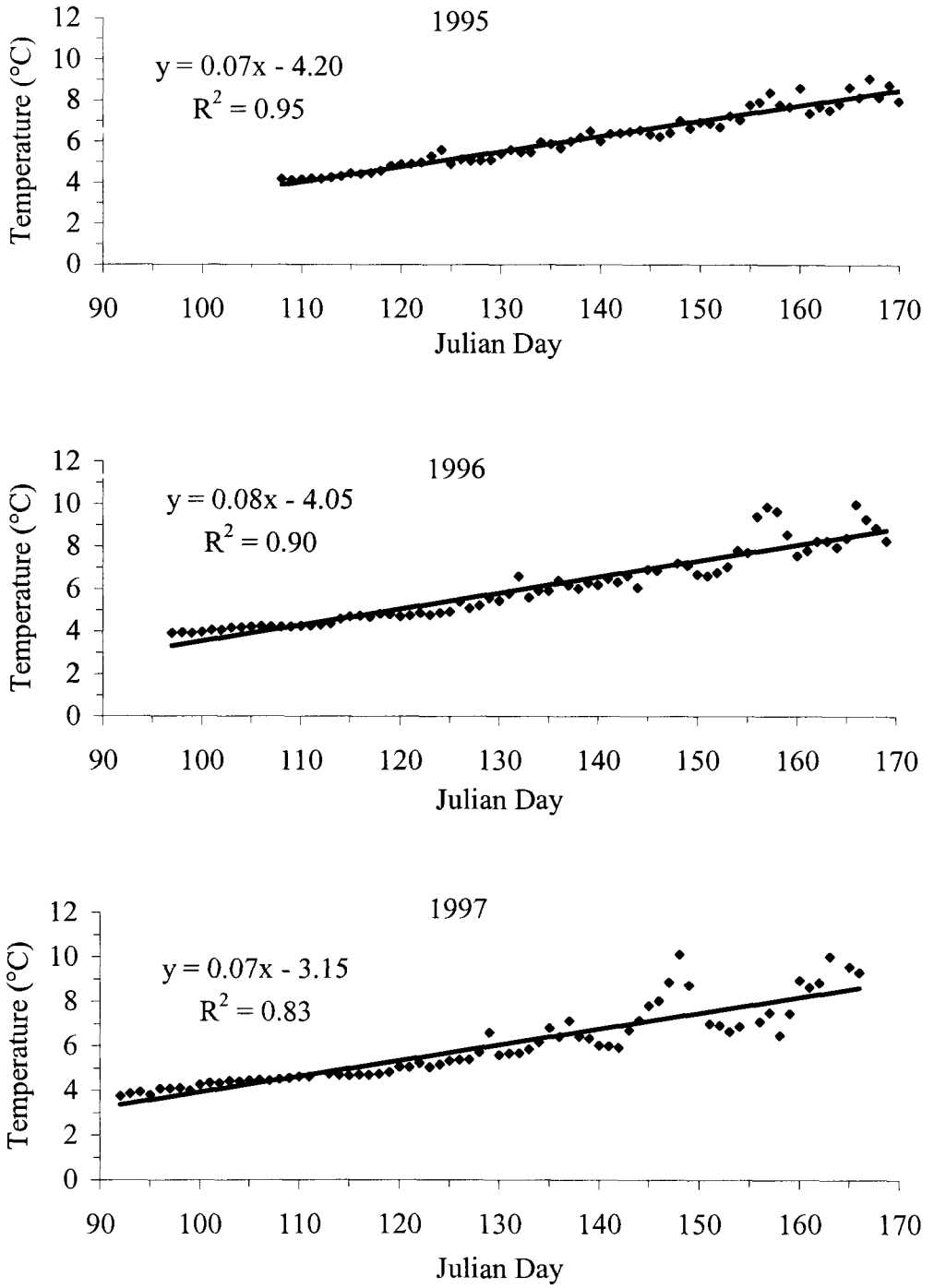

Figure 2. Temperature vs. Julian Day from 5 m for each year.

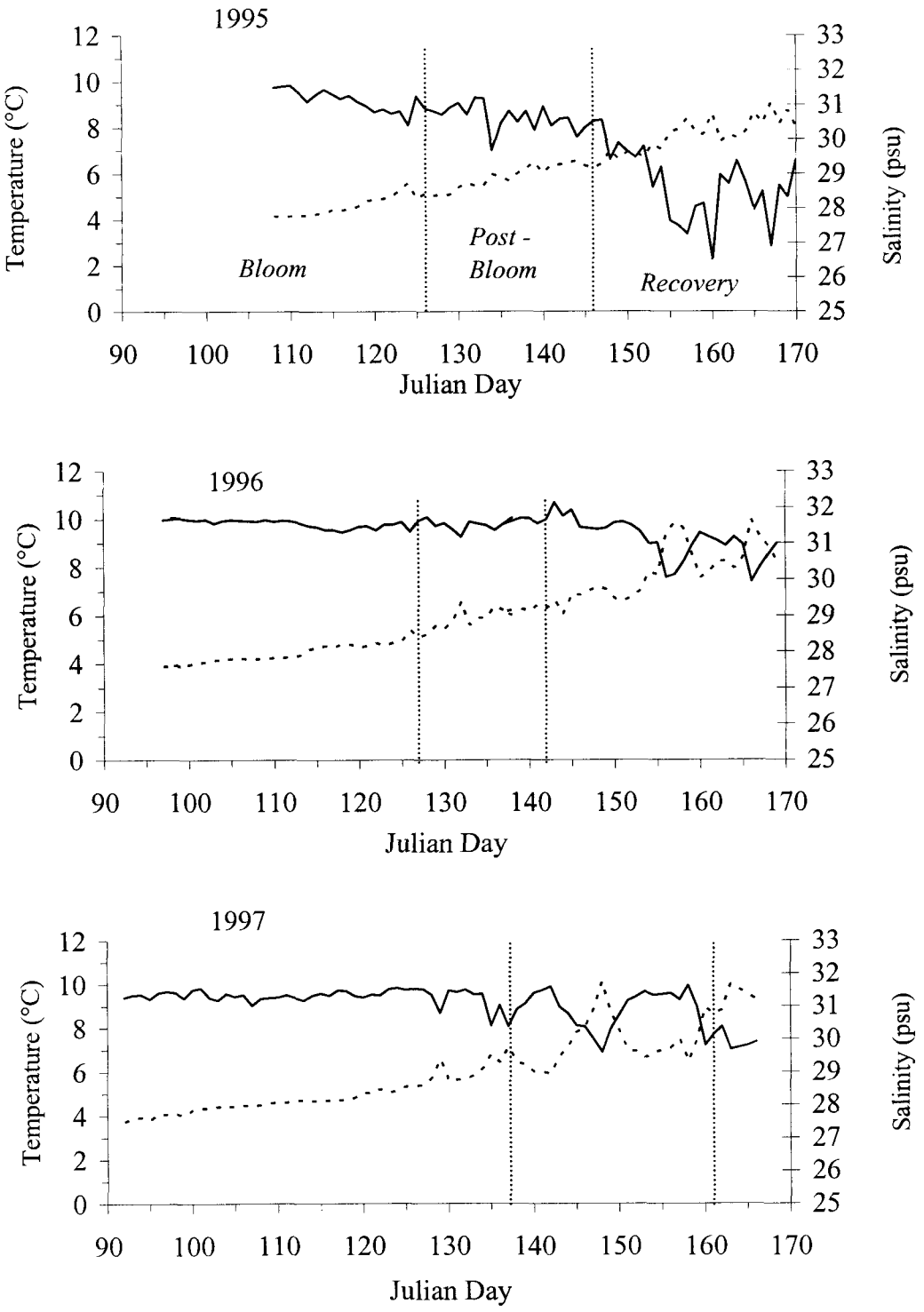

Figure 3. Temperature and salinity from 5 m for each year.
(dashed-temperature; black-salinity)

The mean temperatures were 6.19, 6.01, and 5.92 °C for years 1995, 1996, and 1997, respectively (Table 3). Two Sample Z-Tests suggest that none of the average values were significantly different from each other at $\alpha = 0.05$ significance level (Table 4).

Salinity

In 1995, the mean salinity was 30.0 psu and ranged from 26.5 to 31.6 (Table 3). During the recovery of 1995, salinity values dropped to a minimum of 26.5 psu on day 160 (Figure 3). Values varied slightly but overall they were low for the remainder of the sampling period. The mean salinity in 1996 was 31.4. Salinity values were constant, ranging from 31.2 to 32.1 except for Julian Days 156 and 167. On these two days salinities briefly dropped to 31.1 and 30.3, respectively. The 1997 mean salinity was 31.1 psu with a range of 29.6 to 31.6 psu. Salinity values in 1997 were relatively constant during the spring bloom but varied during the post-bloom and recovery with injections of low salinity water. Two Sample Z-Tests suggest that the mean salinity measurements, from 5 m, of all three years were significantly different at $\alpha = 0.05$ significance level (Table 4).

Nutrients

Nutrient measurements were made on water samples from each sample depth. As for the hydrographic data, the daily values from 5 m are used to characterize the condition in the euphotic zone during each of the sample years. A daily plot of the major nutrient concentrations (N+N, SiO_4 and PO_4) represents the changes in nutrient concentrations for the spring of each year (Figure 4). The initial concentration of N+N

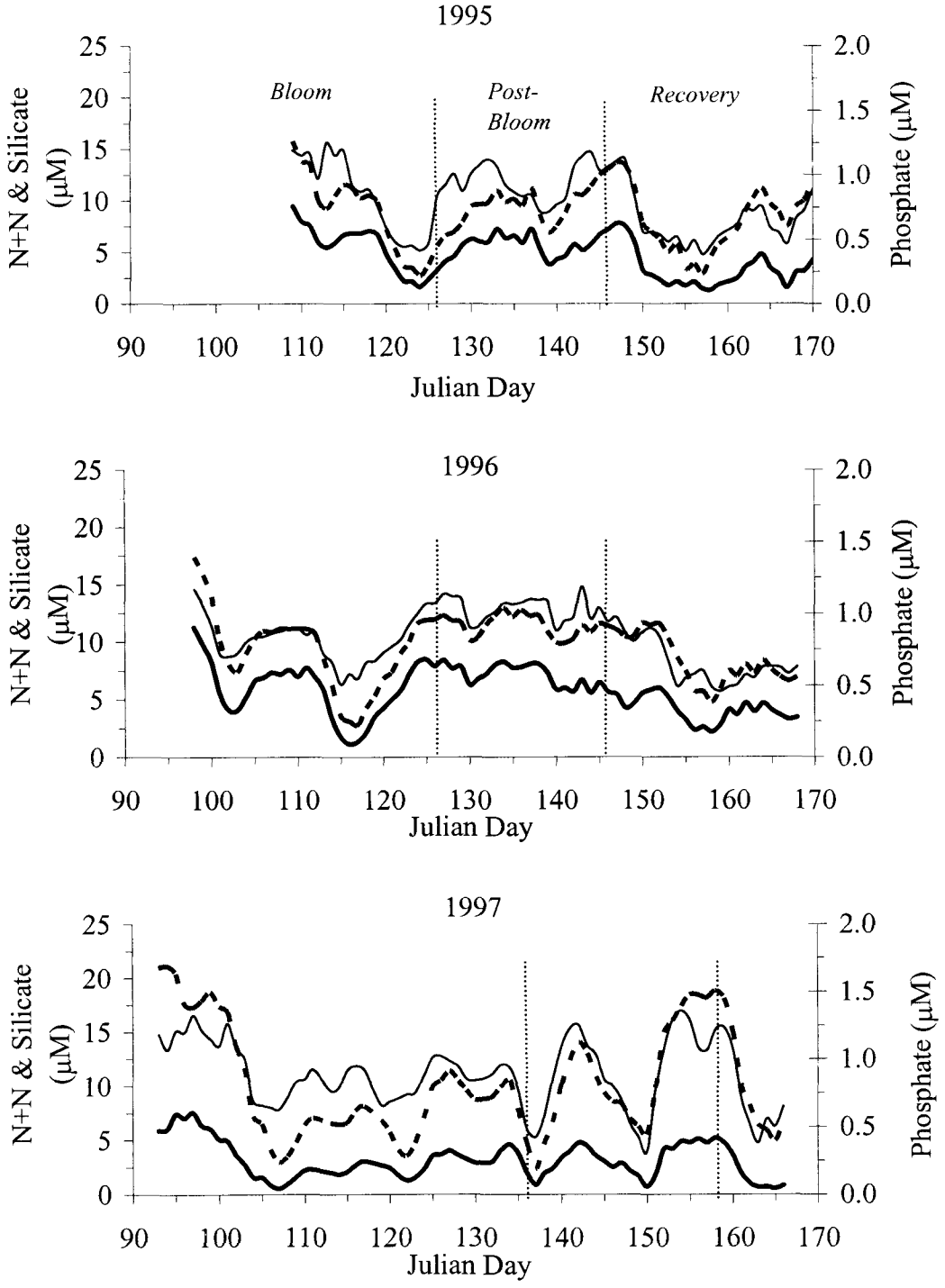

Figure 4. Nutrient concentrations from 5 m with 3 day running mean. (thick black-N+N; dashed-Silicate; thin black-Phosphate)

during the bloom of 1995 was 9.05 μM on day 109. After this day N+N concentrations quickly decreased and reached a minimum (1.17 μM) on day 124. During the post-bloom concentrations rebounded, staying above 2 μM. On day 147 values started to decrease in response to the small increase in phytoplankton biomass during the recovery and on day 151 concentrations reached another minimum of 1.92 μM. The drawdown of nutrients in response to the phytoplankton bloom and recovery observed in 1995 was not as apparent in 1996 or 1997.

The initial concentration of N+N in 1996 was 11.7 μM on day 98. In this year nutrient concentrations in the bloom decreased to 1.04 μM on day 114. After this day values increased and nutrient concentrations remained high until day 156 when the recovery occurred resulting in a decrease in concentration to 0.83μM.

In 1997 the initial concentration of N+N was half the amount of the previous two years (5.79 μM). Concentrations reached a minimum of 0.44 μM on day 106. For the remainder of the sampling season N+N concentrations stayed low but concentrations did fluctuate with injections of nutrients every 14-19 days.

The mean concentrations of N+N were: 4.76 μM for 1995, range 0.0 to 12.27 μM; 5.73 μM for 1996, range 0.83 to 11.72 μM; 3.16 μM for 1997, range 0.24 to 9.22 μM. Two Sample Z-Tests comparing the seasonal means of N+N suggest that the mean values for all three years were significantly different from each other (Table 4).

The patterns of phosphate and silicate concentrations are similar to the N+N concentrations described above. The mean concentrations of phosphate were; 0.81 μM for 1995, range 0.24 to 1.78 μM; 0.83 for 1996, range 0.39 to 1.37 μM; 0.89 μM for

1997, range 0.17 to 1.72 μM. Two Sample Z tests suggest that none of the phosphate means were significantly different from each other.

The mean silicate concentrations were: 8.94 μM for 1995, range 0.37 to 19.75 μM; 9.69 μM for 1996, range 2.24 to 18.15 μM: 10.42 μM for 1997, range 0.88 to 21.64 μM. The mean silicate concentrations were not significantly different from each other (Table 4).

Water Transparency

In general, secchi depths resembled the pattern of integrated chlorophyll (Figure 5). The mean secchi depth during the bloom of each year was 5.67, 4.70, and 6.66 meters for 1995, 1996, and 1997, respectively. During the post-bloom the mean secchi depths were deeper; values were 8.32, 10.38, and 7.26 meters, for each year, respectively. In 1995 and 1997, after the initial increase of chlorophyll during the bloom, the relationship between secchi depth and chlorophyll concentrations did not track as well as they did in 1996. Regressions of integrated chlorophyll vs. secchi depth for each year suggest that secchi depth can explain more than 50% of the variability in the chlorophyll (Figure 6). The r^2 values for the regressions were 0.66, 0.90, and 0.56, respectively, for 1995, 1996, and 1997.

Chlorophyll *a*

In 1995 the spring bloom had already begun on day 107 (Figure 7.). The bloom peaked on day 110 at 431 mg Chl m^{-2}. Chlorophyll values decreased following the bloom and remained low through the post bloom. Chlorophyll values increased during the recovery reaching a maximum value (132 Chl m^{-2}) on day 163. The mean chlorophyll

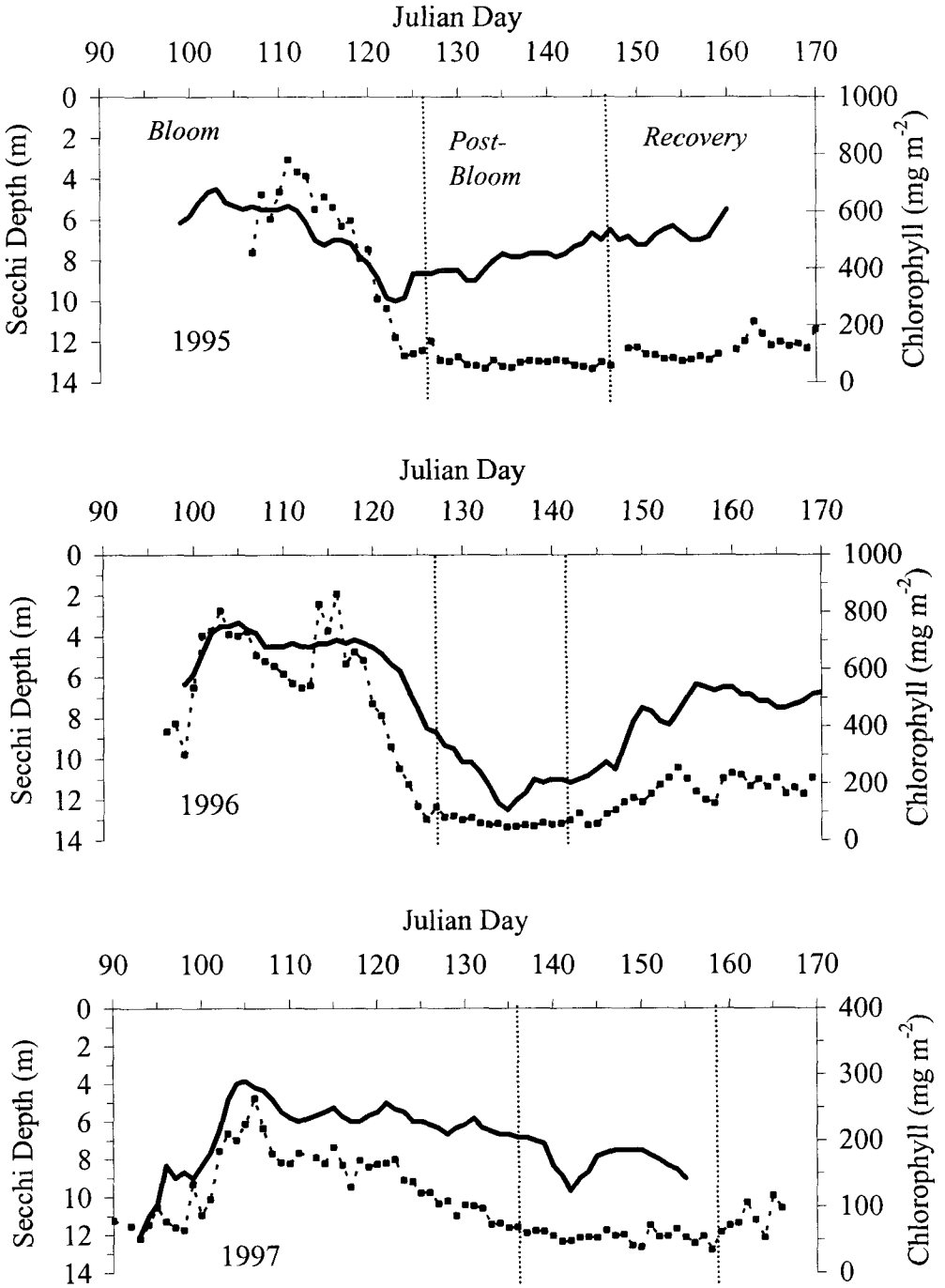

Figure 5. Secchi depth, with 3 day running mean, and integrated chlorophyll (0-25 m) for each year. (dotted-integrated chlorophyll; black- secchi)

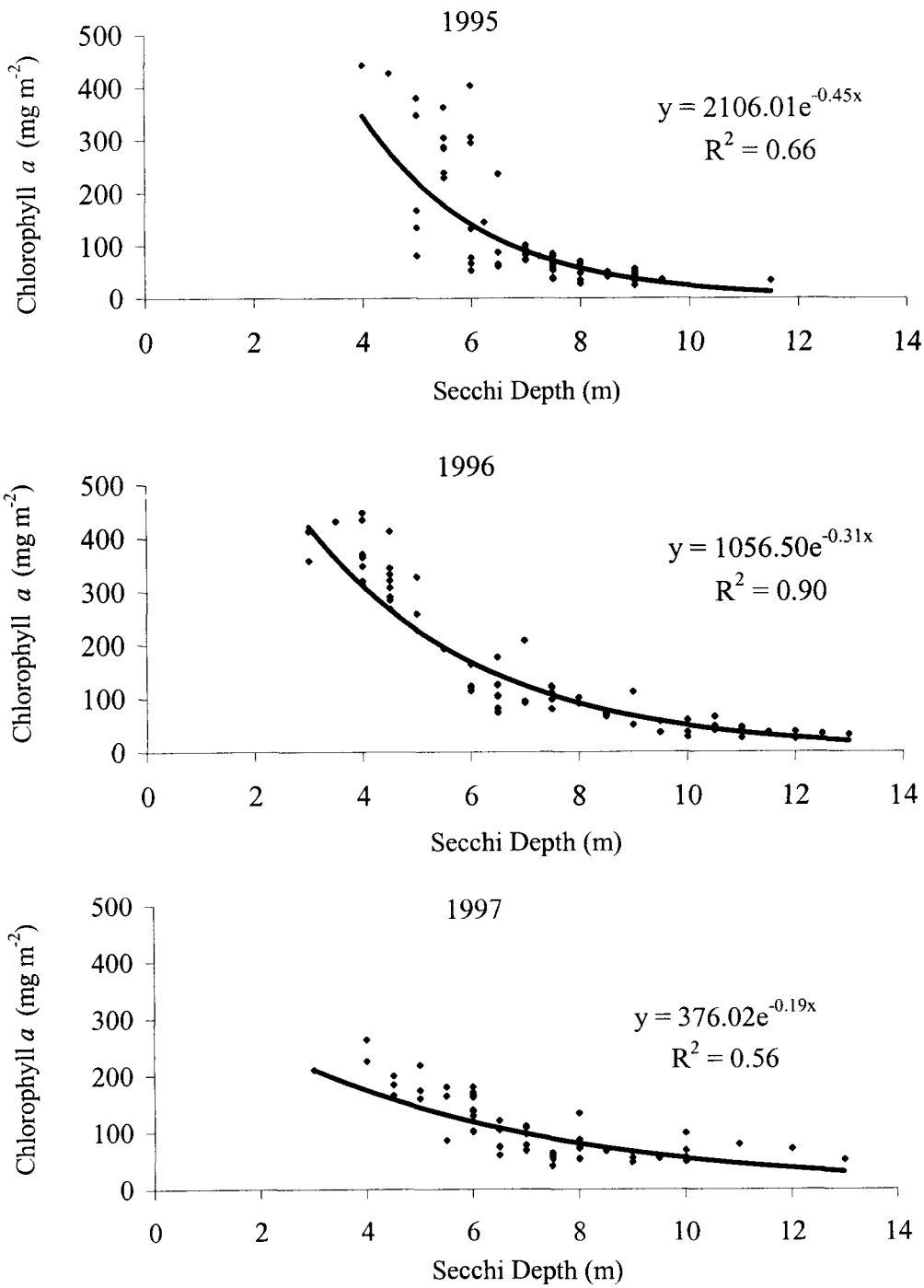

Figure 6. Integrated chlorophyll *a* (0-25 m) vs. secchi depth for the spring of each year.

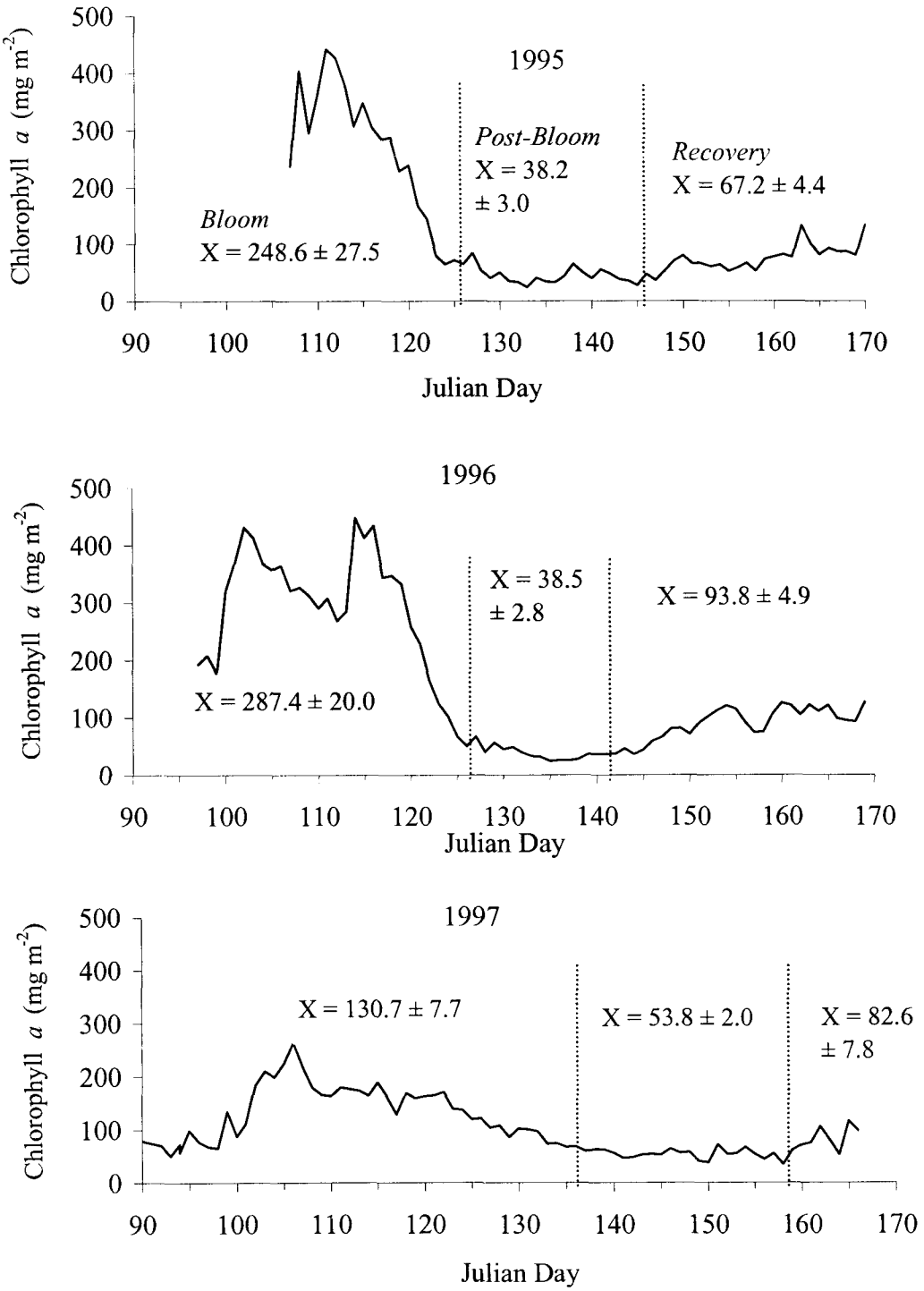

Figure 7. Integrated chlorophyll *a* (0-25 m) for each year.

concentration in 1995, from all available samples, was 5.08 μg l^{-1} and values ranged from 0.56 to 18.85 μg l^{-1} (Table 3).

In 1996 the spring bloom had two peaks; the first occurred on day 107 at 431 mg Chl m^{-2} and the second on day 123 at 448 mg Chl m^{-2}. In this year, after the spring maxima, chlorophyll declined to low values with a minimum of 53 mg Chl m^{-2} on day 135. A recovery occurred later in the sampling season which produced a third of the chlorophyll seen during the bloom. The mean chlorophyll concentration in 1996 was 6.64 μg l^{-1} and values ranged from 0.26 to 19.84 (Table 3.)

In 1997, the bloom was highest on day 106 but biomass was about half the amount (264 mg Chl m^{-2}) of the previous two years. In this year, chlorophyll concentrations decreased gradually after day 106 extending the duration of the bloom. A small recovery began in early June on day 158 with a peak of 16 mg Chl m^{-2} on day 165. The mean chlorophyll concentration in 1997, 4.2 μg l^{-1}, was lower than the means of the previous two years and values ranged from 0.76 to 13.48 μg l^{-1} (Table 3).Two Sample Z-Tests suggest that the seasonal means of chlorophyll from all 3 years were significantly different from each other (Table 4).

Particulate Organic Carbon (POC)

Total particulate organic carbon (POC) samples were collected daily from each depth for each sampling season. The mean concentrations of POC were: 317 μg C l^{-1} for 1995, range 104 to 1028 μg C l^{-1}; 352 μg C l^{-1} for1996, range 109 to 1150 μg C l^{-1}; 251 μg C l^{-1} for 1997, range 91 μg C l^{-1} to 612 μg C l^{-1} (Table 3). Two Sample Z-Tests

comparing the seasonal means of POC suggest that the mean values for all three years were significantly different from each other (Table 4).

Daily POC values were depth averaged (POC_D) to acquire a seasonal trend (Figure 8). The highest concentration of POC_D (610 μg C l^{-1}) in 1995 occurred during the bloom on day 111 and the lowest (174 μg C l^{-1}) occurred on day 145. In 1996, there were two peaks of high POC_D concentration. These peaks occurred on days 103 and 116 with values of 611 and 723 μg C l^{-1}, respectively. In 1996 the lowest POC_D concentration occurred on day 135 at 130 μg C l^{-1}. The POC_D concentrations during the bloom in 1997 were not as high as the previous two years. The maximum concentration of POC_D in this year occurred on day 107 at 537 μg C l^{-1} and the minimum of 121 μg C l^{-1} on day 144.

The 1995 and 1996 average POC_D values were very similar, 344 μg C l^{-1} and 343 μg C l^{-1}, respectively. The 1997 POC_D was lower at 248 μg C l^{-1}. In addition, the seasonal mean of POC_D in 1997 was statistically different than the 1995 and 1996 seasonal means (Table 4).

Particulate Organic Carbon to Chlorophyll (POC:Chl)

The slopes of the linear regressions of POC:Chl for 1995, 1996 and 1997 are 16, 20, and 31, respectively (Figure 9). The variance in POC explained by chlorophyll varied interannually, with values of 31, 47, and 63%, for 1995, 1996, and 1997 respectively. None of the slopes are significantly different from each other at the $\alpha = 0.05$ significance level but the slopes of 1995 and 1997 are significantly different at the $\alpha = 0.10$ significance level (Table 5).

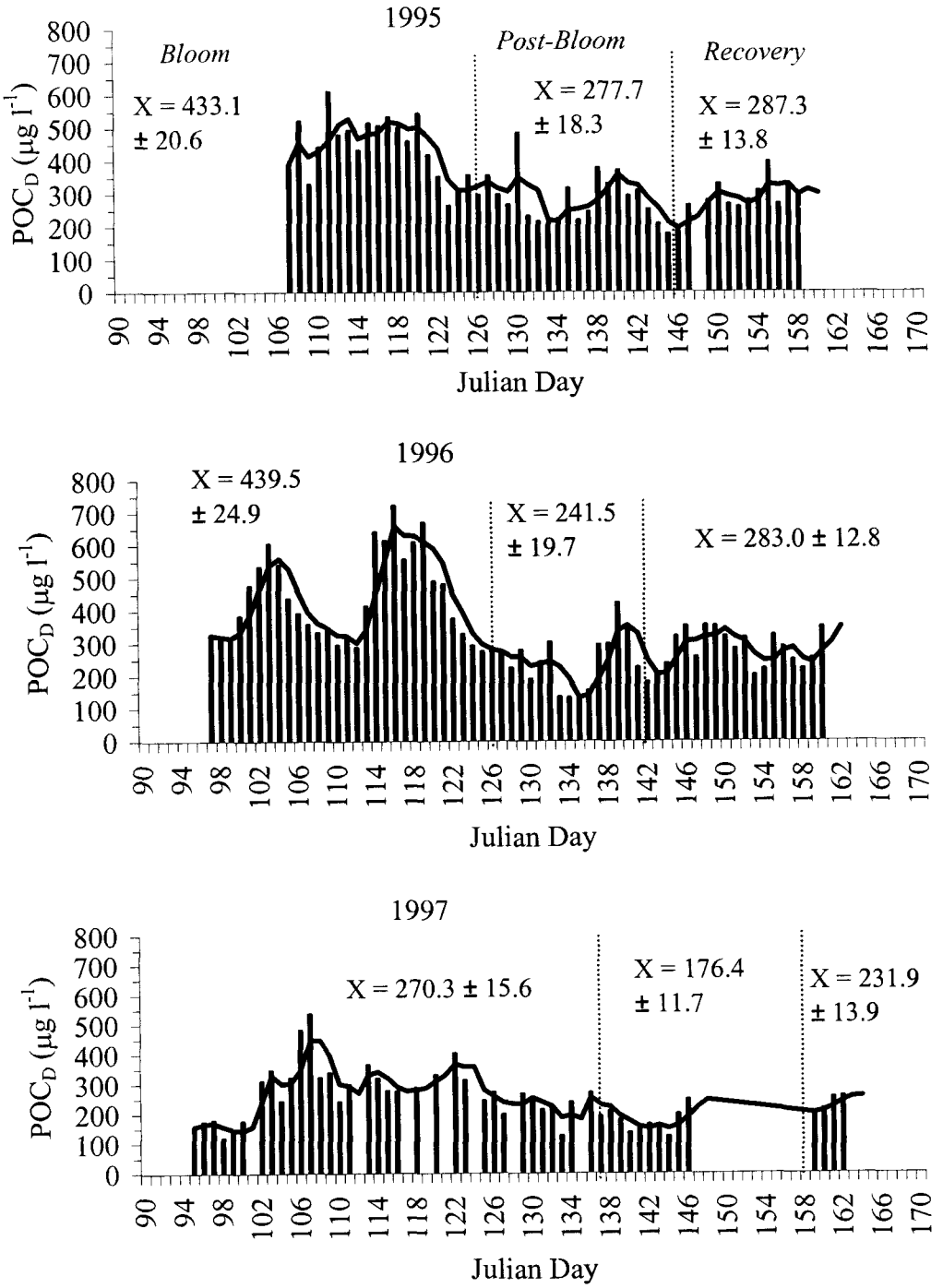

Figure 8. Depth averaged total particulate organic carbon (POC_D) with 3 day running mean.

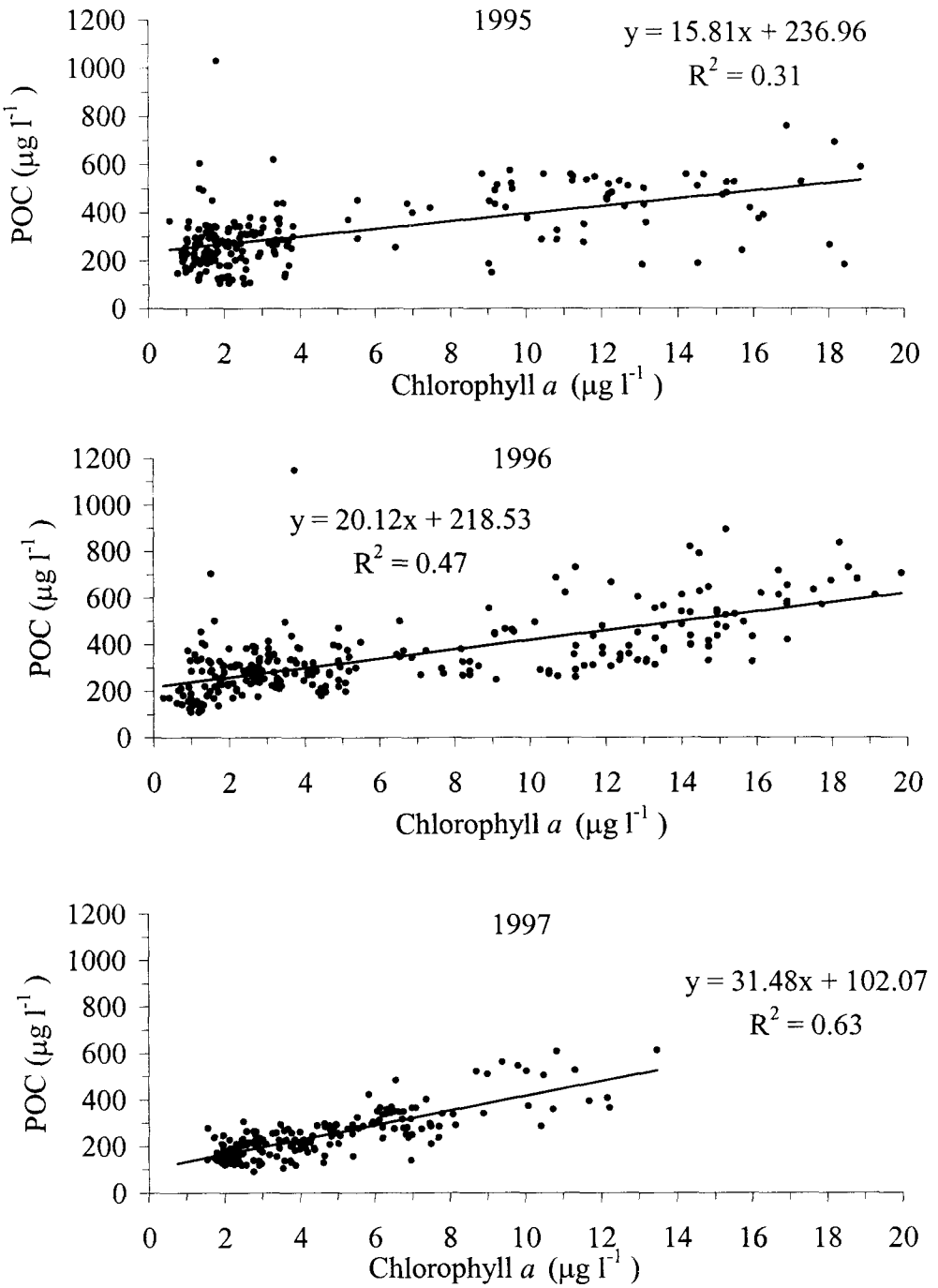

Figure 9. Total particulate organic carbon (POC) in relation to chlorophyll *a* from all sample days and depths for each year.

Table 5. Results from Two Sample T-Tests comparing the slopes of particulate organic carbon to chlorophyll (POC:Chl).

Slope Comparisons	t	
POC vs. Chlorophyll *a*		
95 vs 96	0.39	
95 vs 97	1.60	*
96 vs 97	1.19	

* t calculated from the Two Sample T-Test greater than the critical value 1.28, $\alpha = 0.10$

To compare the seasonal trend of POC:Chl values for each year, the multiple, daily POC:Chl ratios were depth averaged (POC_D:Chl_D) for 0-25 m (Figure 10). In 1995 the POC_D:Chl_D ratios increased after day 125 and stayed relatively high until the end of the sampling season. The pattern of ratios in 1996 revealed a sharp peak on day 139 (POC_D:Chl_D =296). After this date ratios decreased and reached a minimum value of 44 on day 153. The pattern of the POC_D:Chl_D in 1997 is very different than that of the previous two years. The increase in POC_D:Chl_D that began around day 125 in 1995 and 1996 did not occur in 1997, the pattern of POC_D:Chl_D in 1997 is rather uniform; there are no drastic increases or large peaks

The mean values of POC_D:Chl_D for the spring sampling seasons of the 3 years are: 112.5 for 1995, range 27.8 to 241.4; 89.1 for 1996, range 25.4 to 295.7; 58.7 for 1997, range 26.2 to 98.14 (Table 6). Two Sample T-Tests comparing the means for the spring sampling seasons suggest that all the mean ratios are significantly different from each other.

Ratios also varied by the spring sampling time period. The mean POC_D:Chl_D from the bloom of 1996 (41.1) was significantly lower than the mean bloom ratios from

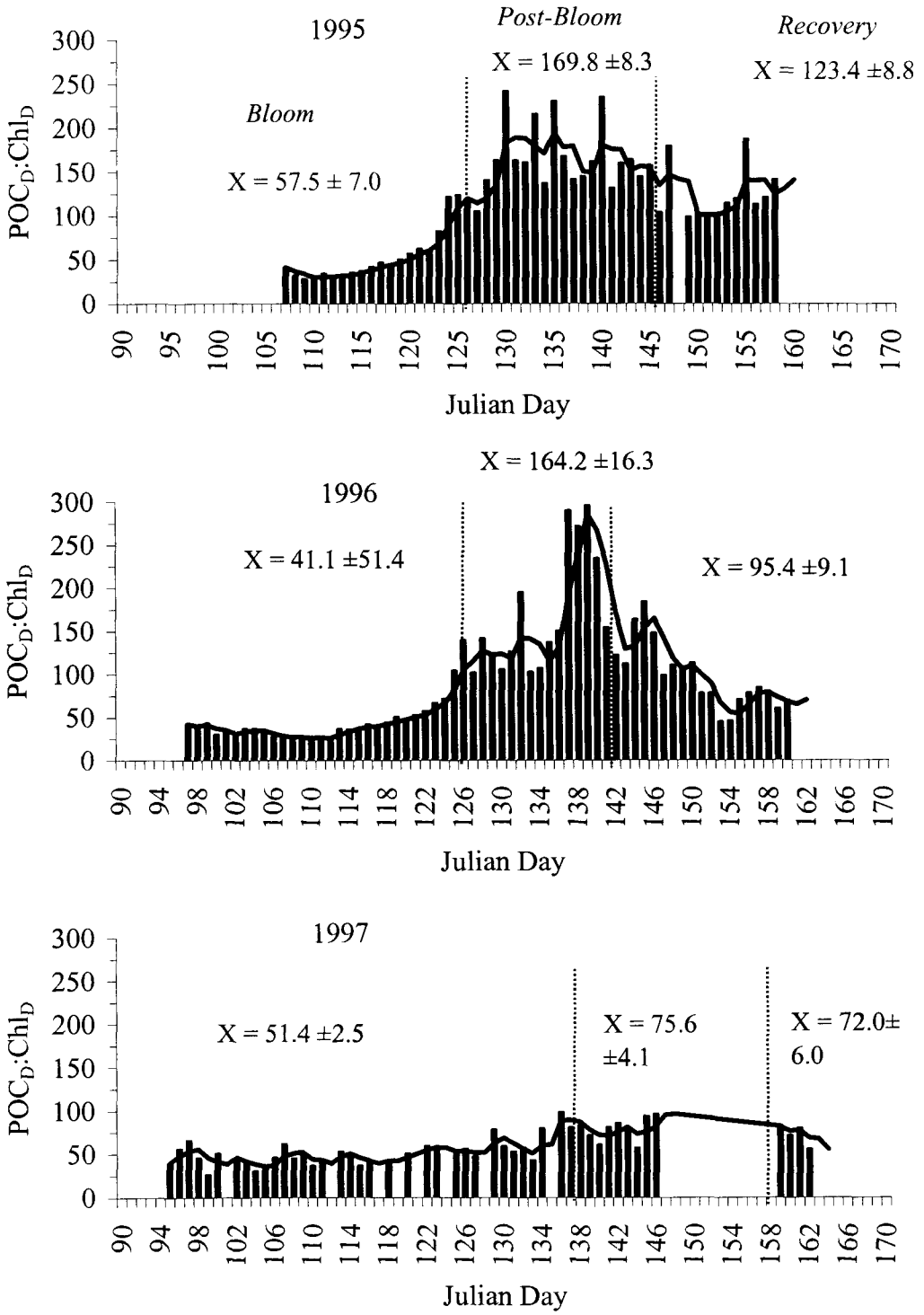

Figure 10. Depth averaged total particulate organic carbon to chlorophyll ratios (POC_D:Chl_D) (0-25 m) with 3 day running mean for each year.

Table 6. Descriptive statistics of depth averaged particulate organic carbon to chlorophyll (POC_D:Chl_D) for each year.

Parameter	1995	1996	1997
Mean ± (SE)	112.54 ± 8.31 *	89.08 ± 8.16 *	58.65 ± 2.58 *
Minimum	27.84	25.41	26.19
Maximum	241.44	295.74	98.14
n	51	64	49

*z calculated from the Two Sample Z-Test greater than the critical value 1.96, $\alpha = 0.05$

Table 7. Average POC_D:Chl_D (± SE) by spring time period.

Year	Bloom	Post-Bloom	Recovery
1995	57.5 ± 7.0	169.8 ± 8.3	123.4 ± 8.8 *
1996	41.1 ± 3.2 *	164.2 ± 16.3	95.4 ± 9.1 *
1997	51.4 ± 2.5	75.6 ± 4.1 *	72.0 ± 6.0 *

*z calculated from the Two Sample Z-Test greater than the critical value 1.96, $\alpha = 0.05$

1995 (57.5) and 1997 (51.4) (Table 7). The mean PCC_D:Chl_D during the post-bloom periods were similar in 1995 (169.8) and 1996 (164.2) but the 1997 post-bloom mean was significantly lower (75.6). The mean recovery ratios for all three years were significantly different from each other: 123.4 for 1995, 95.4 for 1996 and 72.0 for 1997.

Phytoplankton Identification and Enumeration

The species composition of the spring phytoplankton community at this location changed little over the three-year period but relative abundances were different. There were 32 phytoplankton taxa identified for all years of the study (Table 8). The majority of phytoplankton contained in water samples from these three spring season consisted of chain-forming diatoms, flagellates and dinoflagellates. Although the species observed changed little qualitatively from year to year, their abundances varied considerably. In

Table 8. List of phytoplankton taxa collected in the upper 25 m for years 1995 and 1996 (Ward, 1997) and 1997(from this study).

Diatoms

Asterionella glacialic
Biddulphia sp.
Chaetoceros spp.
Ceratium furca
Cocconeis sp.
Chaetoceros deciprens
Cosciondiscus sp.
Eucampia spp.
Fragilariopsis sp.
Leptocylindricus danicus
Leptocylindricus minimus
Leptocylindricus spp.
Licmoophora glacialis
Navicula spp.
Pseudo-Nitaschia spp.
Rhizosolenia fragilissima
Rhizosolenia stolterforthii
Rhizosolenia spp.
Skeletonema costatum
Stephanophyxis nipponica
Thalassiosira spp.
Thalassionema nitzschioides
Unidentified centric diatoms
Unidentified pennate diatoms

Dinoflagellates

Ceratium spp.
Dinophysis spp.
Oxytoxum spp.
Protoperidinium spp.
Unidentified dinoflagellate

Flagellates

Unidentified flagellate
Unidentified silicoflagellate

Other

Ebria tripartita

addition, analysis of species abundance during the different periods of the spring (bloom, post-bloom and recovery) suggests that they were quantitatively different (Table 9).

Table 9. Abundance (% of total) of major phytoplankton taxa by seasonal time period for each year (B = Bloom, PB = Post-Bloom, and R = Recovery).

Taxa	1995			1996			1997		
	B	PB	R	B	PB	R	B	PB	R
Thalassiosira sp.	18.98	0.40	0.52	3.10	0.25	0.10	46.13	10.63	0.53
Stephanophyxis sp.	0.07	0.02	0.00	0.00	0.00	0.00	4.09	0.36	0.00
Nitzschia sp.	4.17	3.23	0.22	4.10	2.21	4.91	2.19	22.18	3.96
Flagaliaropsis sp.	0.00	0.00	0.01	0.30	0.14	0.02	2.59	0.51	0.00
Chaetoceros sp.	6.56	0.73	1.36	19.85	5.43	18.24	24.67	29.47	20.20
Leptocylindrus sp.	2.59	0.34	0.24	0.35	2.26	4.54	0.02	1.17	23.27
Rhizosolenia sp.	0.01	0.02	37.35	0.06	0.82	12.60	0.00	0.02	0.04
Skeletonema costatum	22.51	0.00	0.00	56.77	0.59	2.93	0.64	0.00	0.00
Flagellate sp.	45.11	95.26	60.29	15.46	88.29	56.67	19.68	35.67	52.00

The bloom in 1995 was primarily composed of flagellates (45%). *Skeletonema costatum* constituted 22% of the community and *Thalassiosira* sp. constituted 19%. During the post-bloom flagellate abundance increased to 95%, the diatom *Nitzschia* sp. composed only 3% and the other species were less than 2%. During the recovery flagellate abundance decreased to 60% and the diatom *Rhizosolenia* sp. increased to 37%.

In 1996 the most abundant species during the spring bloom was *Skeletonema costatum,* which composed over half of the community (57%). Other diatoms included *Chaetoceros* sp. (20%), *Nitzschia* sp. (4%), *Thalassiosira* sp. (3%) and flagellates (15%). During the post-bloom flagellate abundance increased to 88% and the diatom *Chaetoceros* sp. decreased to only 5%. In the recovery of 1996 flagellates decreased to 57%, *Rhizosolenia* sp. appeared as it did in 1995 (13%) and Chaetoceros sp. increased to

18%. The remaining 12% of the community consisted of diatoms: *Nitzschia* sp. (5%), *Leptocylindrus* sp. (4%) and *Skeletonema costatum* (3%).

The phytoplankton community during the spring of 1997 was very different from the previous two years. In 1997, *Skeletonema costatum* was rarely seen and *Thalassiosira* sp. was the most abundant taxa composing 46% of the spring bloom community. *Chaetoceros* sp. accounted for 25% and flagellates were only 20%. The remaining bloom community was composed of a low percentage of *Leptocylindrus* sp., *Nitzschia* sp., *Flagaliaropsis* sp. and for the first time in this study, *Stephanophyxis* sp. During the post-bloom *Thalassiosira* sp. abundance decreased to 11% and, as seen in the previous two years, the flagellate population increased but only to 36%. Unlike the previous two years diatom abundances stayed high during the post-bloom; *Chaetoceros* sp. increased to 29% and *Nitzschia* sp. to 22%. The recovery community in 1997 was a departure from that which occurred in the previous two years. The formerly dominant diatom *Rhizosolenia* sp. was nearly absent from all samples and was replaced by *Chaetoceros* sp. and *Leptocylindrus* sp. *Thalassiosira* sp. decreased to 0.5%, *Chaetoceros* sp. accounted for 20%, *Leptocylindrus* sp. increased to 23% and flagellates increased to 52%.

A comparison of the phytoplankton community characteristics, based on mean values, indicates that the 1996 and 1997 communities were distinct (Figure 11 and Table 4). In 1996, there were significantly more phytoplankton cells (5496 cells ml^{-1}) than in 1995 (858 cells ml^{-1}) and 1997 (1926 cells ml^{-1}) (Figure 11.b). Although there were more cells in 1996 the mean cell size (455 μm^3 $cell^{-1}$) was significantly smaller than the mean in 1997 (2291 μm^3 $cell^{-1}$) (Figure 11.a). In addition, the mean concentration of carbon

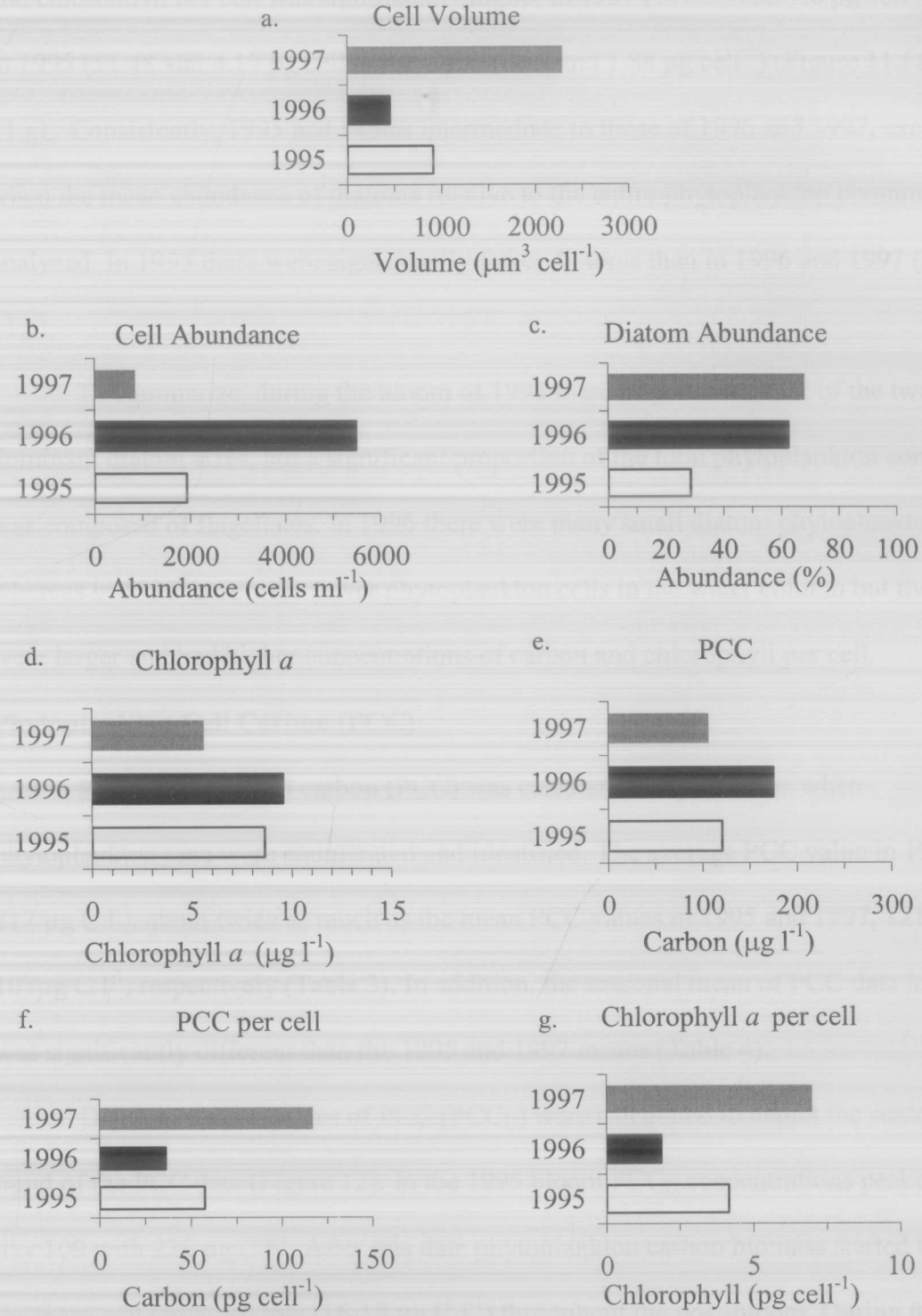

Figure 11. Comparisons of average phytoplankton community characteristics in the spring.

and chlorophyll per cell was significantly higher in 1997 (117.25 and 7.0 pg $cell^{-1}$) than in 1995 (51.48 and 4.17 pg $cell^{-1}$) and 1996 (36.2 and 1.88 pg $cell^{-1}$) (Figure 11.f and 11.g). Consistently, 1995 had values intermediate to those of 1996 and 1997, except when the mean abundance of diatoms relative to the entire phytoplankton community was analyzed. In 1995 there were significantly fewer diatoms than in 1996 and 1997 (Figure 11.c).

To summarize, during the bloom of 1995 there was an even mix of the two dominant diatom sizes, but a significant proportion of the total phytoplankton community was composed of flagellates. In 1996 there were many small diatom phytoplankton cells whereas in 1997 there were fewer phytoplankton cells in the water column but these cells were larger and had higher concentrations of carbon and chlorophyll per cell.

Phytoplankton Cell Carbon (PCC)

Phytoplankton cell carbon (PCC) was calculated only on dates when phytoplankton taxa were enumerated and identified. The average PCC value in 1996 was 217 $\mu g\ C\ l^{-1}$, about twice as much as the mean PCC values in 1995 and 1997, 121 and 107$\mu g\ C\ l^{-1}$, respectively (Table 3). In addition, the seasonal mean of PCC data in 1996 was significantly different than the 1995 and 1997 means (Table 4).

Depth averaged values of PCC (PCC_D) were calculated to depict the seasonal trend of the PCC data (Figure 12). In the 1995 bloom PCC_D concentrations peaked on day 109 with 226 $\mu g\ C\ l^{-1}$. After this date phytoplankton carbon biomass started to decrease and remained low (16-18 $\mu g\ C\ l^{-1}$) throughout the post-bloom. During the recovery PCC_D values increased to 86 $\mu g\ C\ l^{-1}$ on day 164. PCC during the bloom of

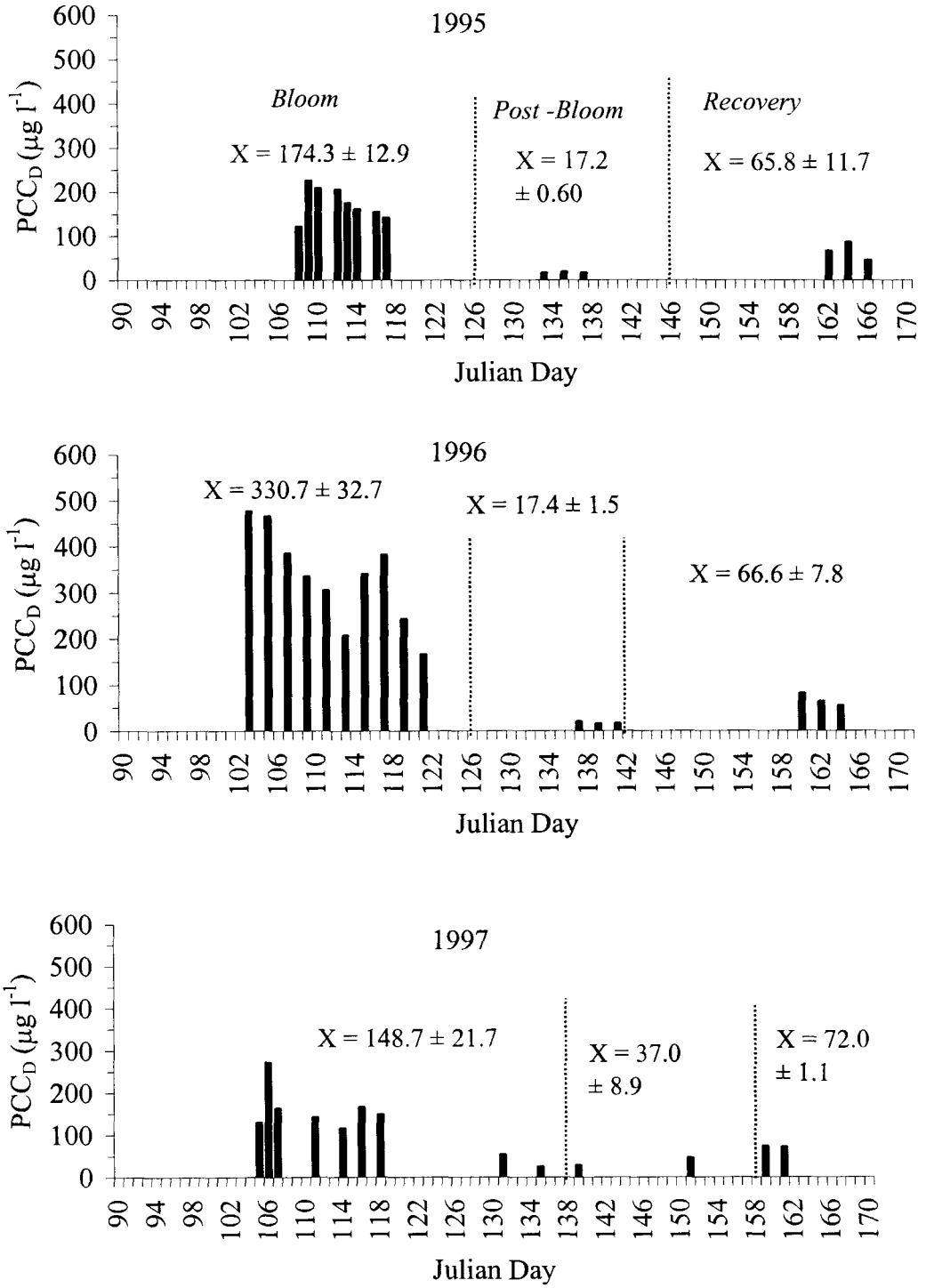

Figure 12. Depth averaged phytoplankton cell carbon (PCC_D).

1996 was much higher than in the other two study years. The highest value (477 μg C l^{-1}) was measured on day 102. After day 102, a decline occurred until day 112 when concentrations increased and a second peak of 382 μg C l^{-1} occurred on day 116. In the post-bloom PCC_D values decreased as in the previous year to 16 μg C l^{-1} on day 140 and values increased during the recovery, with 81 μg C l^{-1} measured on day 159.

In 1997 the highest concentration of PCC_D (272 μg C l^{-1}) occurred on day 106. During the post-bloom biomass decreased as in the previous two years but PCC_D concentrations were higher, never dropping below 25 μg C l^{-1}. During the recovery PCC_D values increased to 73 μg C l^{-1} on day 159.

The amount of PCC contributed by the most abundant taxa varied from year to year (Figure 13). In 1995, *Thalassiosira* sp. was 58% of phytoplankton carbon. flagellates, *Skeletonema costatum*, and *Rhizosolenia* sp. all contributed similar amounts, 17, 13, and 10%, respectively. In 1996, the most abundant taxon during the spring bloom, *S. costatum*, composed 58% of the PCC. *Thalassiosira* sp., flagellates, and *Rhizosolenia* sp. contributed 18, 10, and 3%, respectively. In 1997, *Thalassiosira* sp. constituted 68%, flagellates 13%, *Leptocylindrus* sp. and *Stephanophyxis nipponica* constituted 7% and 6%, respectively.

Phytoplankton Cell Carbon to Chlorophyll (PCC:Chl)

The slopes of the linear regressions of PCC:Chl for 1995, 1996 and 1997 are 12, 24, and 21, respectively (Figure 14). The variance in PCC that can be explained by chlorophyll is consistent from year to year, 74-76%. Two Sample T-Tests comparing the slopes of all years suggest that none of the slopes are statistically different (Table 10). As

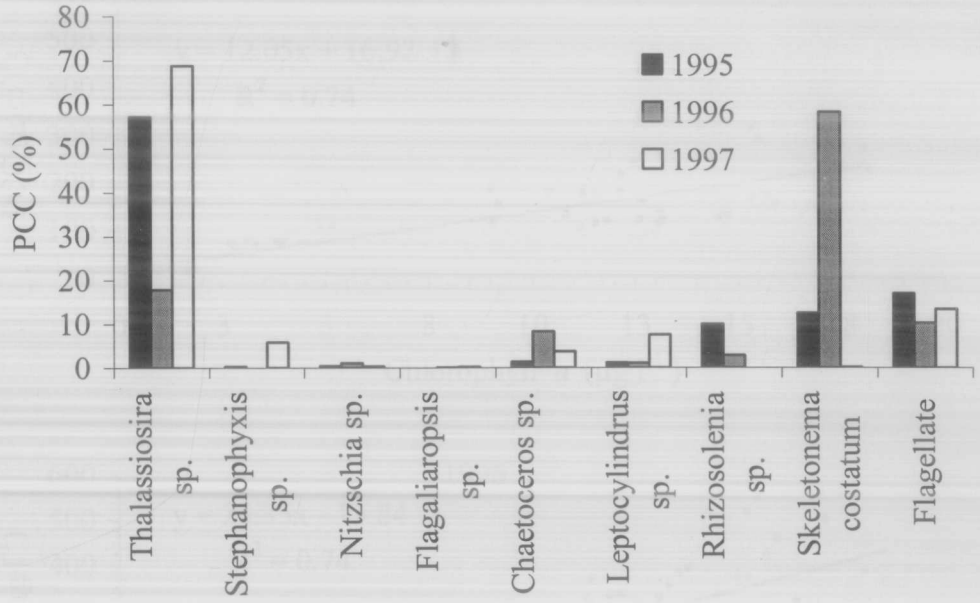

Figure 13. Contributions by individual phytoplankton taxa to total PCC for each year.

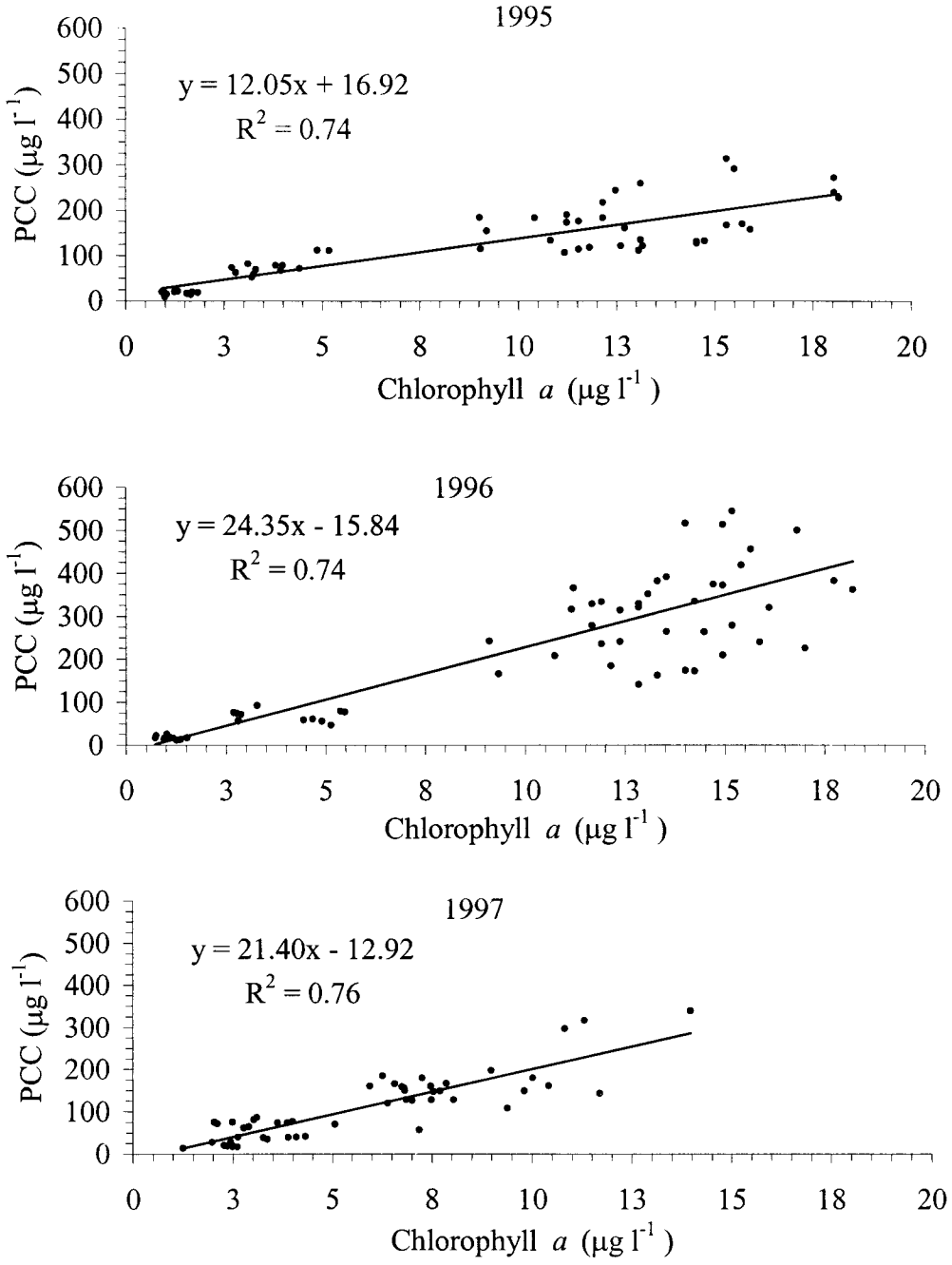

Figure 14. Phytoplankton cell carbon (PCC) in relation to chlorophyll *a* for all sample days and depths of each year.

Table 10. Results from Two Sample T-Tests comparing the slopes of phytoplankton cell carbon to chlorophyll (PCC:Chl) for each year.

Slope Comparisions	t
PCC vs. Chlorophyll *a*	
95 vs 96	0.98
95 vs 97	1.21
96 vs 97	0.24

with the POC:Chl data, the PCC:Chl ratios were depth averaged, from 0-25 m, to compare the temporal trend of the ratios (Figure 15). The mean values of PCC_D:Chl_D were: 14.2 for1995, range 7.5 to 21.6; 20.0 for 1996, range 11.1 to 31.6; 20.6 for 1997, range 11 to 31.1 (Table 11). Two Sample T-Tests comparing the means for the spring sampling seasons suggest that the mean of 1995 is significantly different the 1996 and 1997 means.

Ratios also varied by the spring sampling time period. In the bloom of 1995 the mean PCC_D:Chl_D (12.9) was significantly lower than the mean ratios during the bloom in the following two years (23.2 for 1996, 20.8 for 1997) (Table 12). The mean PCC_D:Chl_D during the post-bloom periods were all similar, 13.4, 15.0, and 13.6 for 1995, 1996, and 1997, respectively. In addition, none of the ratios were significantly different from each other. The mean ratio during the recovery in 1997 (26.6) was significantly higher than the mean ratios during this time period in 1995 and 1996.

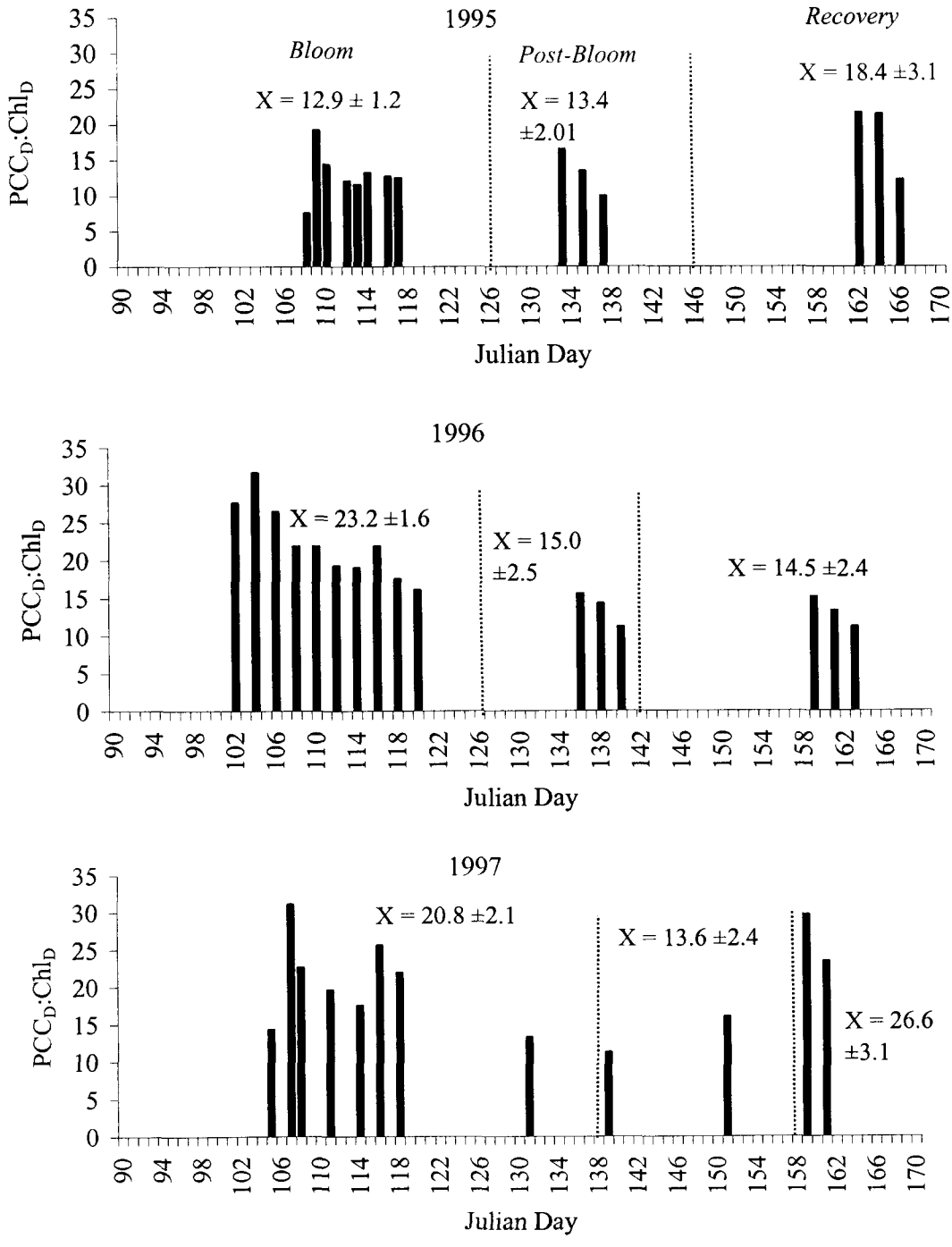

Figure 15. Depth averaged phytoplankton cell carbon to chlorophyll (PCC_D:Chl_D) (0-25 m).

Table 11. Descriptive statistics of depth averaged phytoplankton cell carbon to chlorophyll (PCC_D:Chl_D) for each year.

Parameter	1995	1996	1997
PCC_D:Chl_D			
Mean ± (SE)	14.16 ± 1.11 *	20.01 ± 1.54	20.55 ± 1.83
Minimum	7.50	11.14	11.23
Maximum	21.61	31.63	31.15
n	14	16	12

*indicates mean significantly different from others; t calculated from the Two Sample T-Test greater than the critical value 1.96, α=0.05

Table 12. Average PCC_D:Chl_D (± SE) by spring time period.

Year	Bloom	Post-Bloom	Recovery
1995	12.9 ± 1.2 *	13.4 ± 2.01	18.4 ±3.10
1996	23.2 ± 1.6	15.0 ± 2.5	14.5 ± 2.4
1997	20.8 ± 2.1	13.6 ± 2.38	26.6 ± 3.13 *

*indicates mean significantly different from others; t calculated from the Two Sample T-Test greater than the critical value 1.96, α=0.05

DISCUSSION

This study is an investigation into the carbon to chlorophyll ratio of phytoplankton during the spring bloom in Prince William Sound, Alaska. This ratio was investigated for three seasons using two direct methods, and these results were compared to a "best guess" fixed ratio value taken from the literature. Since the latter is often used in carbon budgets and model calculations a comparison with more accurate, direct measurements provides an estimate of its accuracy and appropriateness for use in coastal Gulf of Alaska waters. Chlorophyll is routinely measured by biological oceanographers as an estimate of phytoplankton biomass but the translation to carbon biomass, the preferred parameter, is enigmatic.

The first method, the easiest and most often used, compares bulk organic carbon, after filtering for removal of larger particles, with total chlorophyll of the same water sample. Such a technique will vary as an estimate of plant carbon depending on the quantity of non-plant particles present in the water sample. The other technique is a nearly direct measure of the carbon associated with phytoplankton cells. It is obtained by identification, enumeration and size determination of the phytoplankton in a sample; the carbon is then calculated from a set of equations from literature studies appropriate to the taxa that estimate the carbon content of cell plasma. For comparison to these two techniques a fixed ratio of 30:1 was used. This fixed ratio was chosen based on Taylor et al. (1997) who suggested that C:Chl varies from 20-40 at 60°N, and from Riemann et al.(1989) who found C:Chl values of 27-67 in natural populations. My original hypothesis, that there are significant interannual differences in the spring PCC:Chl, based

on the average ratio determined by linear regression, was not supported by the data. However, this research has indicated that the ratio is primarily determined by the species composition of the phytoplankton community rather than external factors that influence phytoplankton productivity. In addition, this research indicates that the identification and enumeration method, although rarely used because it is the most time and labor intensive, is the closest to a true estimate of phytoplankton carbon.

Comparison of Carbon Biomass Values

Comparison of the different methods used to estimate phytoplankton carbon produced biomass values with considerable variation (Figure 16). In each year the amount of carbon estimated by POC:Chl was the greatest of the three methods. The fixed conversion factor (C:Chl = 30) was intermediate and the PCC:Chl was the lowest. In 1996 and 1997, the three ratios were somewhat similar in the early bloom but values based on POC:Chl values became higher as the season progressed. In 1995, the POC:Chl and fixed ratio values of carbon were similar at the very beginning of the season but after day 113 the POC:Chl values were notably higher for the remainder of the sampling season. After this date the fixed ratio values decreased quickly and tracked very closely to the PCC:Chl values of carbon for the remainder of the season.

In 1996 all three ratios were similar until day 116. After this day the PCC:Chl and fixed ratio values decreased and tracked closely as they did in 1995 but the POC:Chl remained notably higher. All three of the methods estimated less carbon biomass in 1997 than in the previous two years. In this year POC:Chl did not track the other two methods

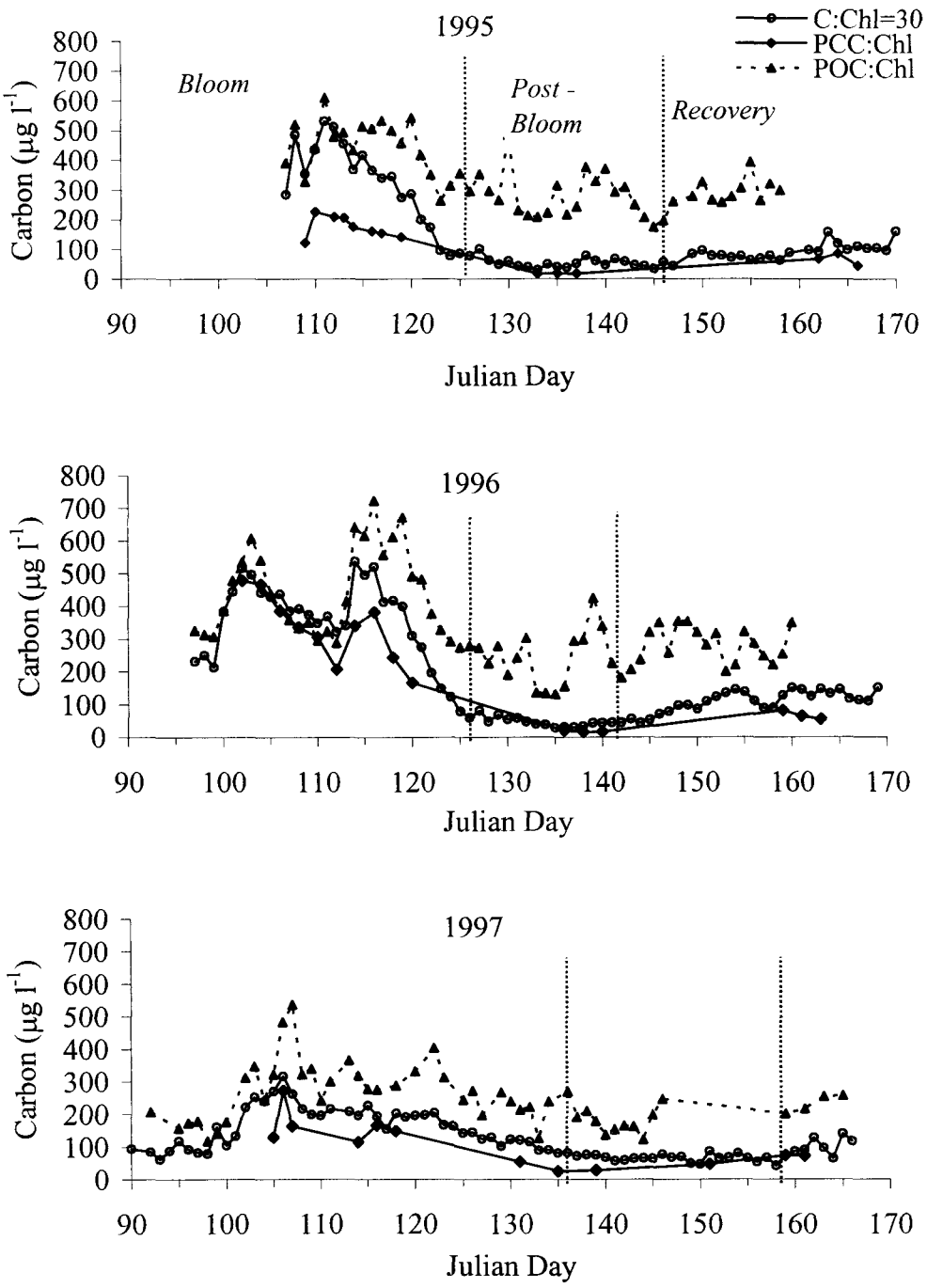

Figure 16. Comparison of phytoplankton carbon values by three different methods: fixed ratio (C:Chl = 30), PCC:Chl, and POC:Chl.

very well; it consistently projected a higher biomass. PCC:Chl and the fixed ratio had a similar pattern, tracking closely for the entire sampling season.

A summary of the three methods used shows that the range of phytoplankton carbon biomass estimates for POC:Chl was greater than the PCC:Chl and the fixed ratio (Table 13). The mean values (for all years) produced by these methods were all significantly different. POC:Chl had the highest mean estimate (155.6) and the fixed ratio of 30 the second highest (75.4). The mean carbon biomass estimate using the PCC:Chl ratio (18.4), is much lower but appears to be a more reasonable estimate of the phytoplankton biomass for this location in Prince William Sound.

Table 13. Summary of phytoplankton carbon biomass estimates.

	Fixed Ratio (30)	POC:Chl	PCC:Chl
Slope	N/A	16, 20, 31	12,24,21
Range	29 - 537	13 - 516	6 - 39
Mean	155.6 ± 8.9 *	75.4 ± 7.0 *	18.4 ± 0.56 *

*t calculated from the Two Sample T-Test greater than the critical value 1.96, α=0.05

Effect of Species Composition on C:Chl

Nutrients are abundant in the beginning of the bloom and available for uptake and growth by the phytoplankton. As the bloom progresses nutrients decline and zooplankton begin their migration from depth to the surface in late May (Cooney and Coyle 1996). The combination of declining nutrients and an increase in zooplankton biomass ultimately effects species composition. Nutrient and chlorophyll data from this study in conjunction with corresponding zooplankton data (Eslinger et al. 2001) suggest that

zooplankton grazing influences phytoplankton biomass and species composition since there is minor response to the nutrient pulses following the bloom (Figure 17).

Although the PCC:Chl ratios estimated from linear regression were not significantly different, data acquired from microscopic analysis of the phytoplankton community revealed that the phytoplankton community composing the PCC:Chl ratios was very different. The dominant species during the bloom of 1997 was *Thalassiosira* sp., a larger centric diatom that averaged 32.32 μm in diameter with a mean carbon concentration of 452.93 pg $cell^{-1}$. The dominant species in 1996, *Skeletonema costatum,* averaged 13 μm in diameter and its mean carbon concentration was 44.63 pg $cell^{-1}$. In 1995 there was an even mix of the two previously mentioned diatoms as well as a significant amount of flagellates which averaged 18 pg $cell^{-1}$. This variation in species composition is very important in terms of bioenergetics. As stated by Booth and Smith (1997), information regarding phytoplankton cell size is critical for biogeochemical cycles. The differences in cell size, taste and digestibility all have a major affect on the available food source to heterotrophic plankton. Although the ratios of PCC:Chl are not significantly different from 1996 and 1997, the *type* of biomass was not the same. This information would not have been known without taxonomic analysis of the phytoplankton community. Although it is very time consuming and tedious, microscope analysis is crucial in explaining carbon production and food web linkages.

Particulate Organic Carbon (POC)

A major disadvantage to using POC as an estimate for phytoplankton carbon is the addition of multiple types of carbon biomass into the estimate. According to

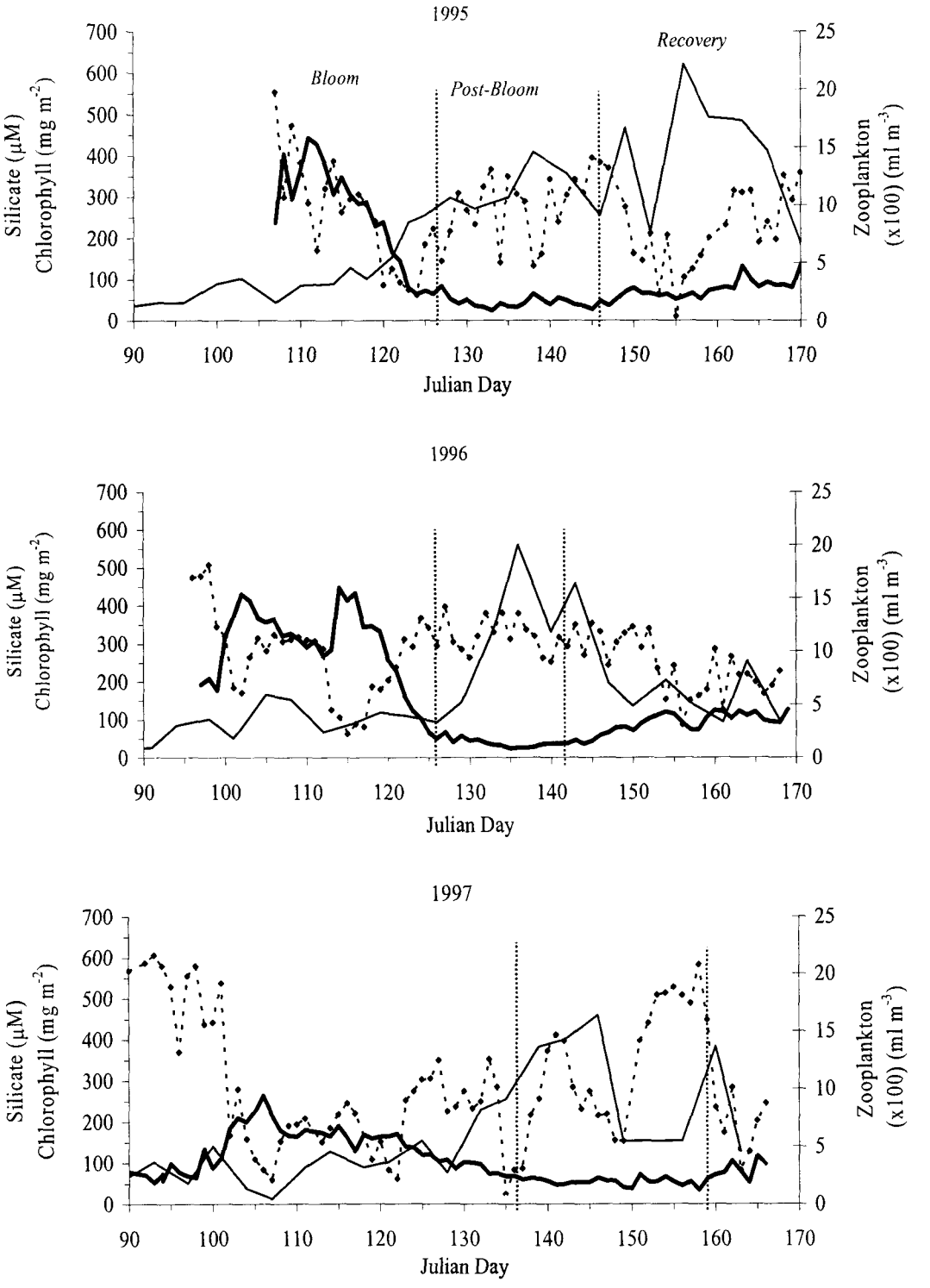

Figure 17. Integrated chlorophyll (0-25 m), silicate concentration from 5 m, and zooplankton (settled volume) (Eslinger et al., 2001) for each year. (thick black-chlorophyll; dashed-silicate; thin black-zooplankton)

Taylor et al. (1997), POC can not be directly compared with chlorophyll due to the varied composition of phytoplankton carbon in POC. In some areas eukaryotic phytoplankton have been shown to account for a significant portion of the POC but in other areas bacterial carbon has been shown to compose a high proportion of the POC (Andersson and Rudehäll 1993).

Concentrations and trends of POC from this study are in good agreement with results for other higher latitude spring bloom values (e.g. Andersson and Rudehäll 1993). The highest concentrations of POC occurred during the peak of the spring bloom and decreased as summer progressed. The range of POC values reported by Andersson and Rudehäll (161-668 $\mu g\ C\ l^{-1}$) are similar to the values (91-1150 $\mu g\ C\ l^{-1}$) from this study.

The average POC in 1997 was significantly lower than the averages of 1995 and 1996. Differences in POC by year and time period were evident as well. In 1997, during the bloom, the average POC concentration was about half the amount measured in 1995 and 1996. The POC mean during the post-bloom was again lower in 1997 but the recovery mean was similar to the means of the previous two years.

Particulate Organic Carbon to Chlorophyll (POC:Chl)

There was a statistically significant variation in the bulk ratio of POC:Chl between years; the averages were 112, 89 and 59 for 1995, 1996, and 1997, respectively, and the range for all years was 25.4 to 295.6. The average bloom ratios for all years were similar but the ratios for the post-bloom and recovery were variable. The bloom ratios were 57.5, 41.1, and 51.4, respectively for 1995, 1996, and 1997. The post-bloom average ratios of 1995 and 1996 were very similar, 169.8 and 164.2, respectively, but in

1997 the average ratio, 75.6, was half the means of the previous two years. The average recovery ratios declined progressively from a high of 123.4 in 1995 to 95.4 in 1996 and 72.0 in 1997. There was virtually no difference in the post-bloom and recovery ratios in 1997 and they were much lower than the previous two years. The high POC:Chl ratios in 1995 and 1996 suggest that the particulate organic carbon in these two years was composed of more detrital or non-plant carbon than in 1997.

The slope of the regression line of POC vs. chlorophyll should reflect the average ratio of the POC that is associated with the chlorophyll (Banse, 1977) and thus is another way to express the C:Chl ratio. The average ratios estimated by regressing POC and Chl were 16, 20, and 31 respectively for 1995, 1996, and 1997 (Figure 9). Two Sample T-Tests ($\alpha = 0.10$) suggest that the slopes of POC:Chl were significantly different for 1995 and 1997. The higher r^2 (0.63) from the regression of POC and chlorophyll for 1997 suggests that there is more plant carbon associated with the POC in 1997 than in the previous two years.

Phytoplankton Cell Carbon (PCC)

Phytoplankton cell carbon is a calculation based on the plasma volume in a cell, which is estimated from cell size measurements and equations relevant to the taxa (e.g. diatoms, flagellates etc. see p.14) being measured. The estimates are scaled up to sample volumes from species specific cell counts in a 50 ml subsample preserved from the original water samples. Errors related to this aspect of the method are due to the possibility of errors in species composition resulting from insufficient counts, and the representative nature of the subsample. Preservation of fragile species is also a problem,

and such groups may be underrepresented in stored samples. The determination of PCC from microscopy, although previously stated as being considered the most reliable, does have multiple sources of associated error. One source of variation in the PCC values between studies may be a result of the selected biovolume conversion method (Jasprica and Caríc 1997). Biovolume conversion methods have been developed by Strathman (1967), Booth et al. (1993), Montagnes and Berge (1994) and Verity et al. (1992). In addition, due to the difficulty in accurately measuring species lengths and widths, miscalculations can occur for species average dimensions. Nonetheless, the estimate of phytoplankton cell carbon from cell enumeration and measurement is specific to phytoplankton and thus eliminates the complications of animal or detrital carbon.

The mean values of PCC were 121 ($\mu g\ C\ l^{-1}$), 217 and 107, respectively, for 1995, 1996, and 1997.The mean PCC values from 1995 and 1997 are in the range of values from Andersson & Rudehäll's (1993) study of the Baltic Sea (90-200 $\mu g\ C\ l^{-1}$, dependent on station). Although, the mean PCC in 1996 is in the range of values (6-417$\mu g\ C\ l^{-1}$) from Booth and Smith (1997), the very high ratios from the 1996 data were greater than values found in either of the two studies previously mentioned.

The mean PCC of 1996 was significantly higher than the 1995 and 1997 means. This may be due to the very high concentration of PCC during the bloom of 1996 (330.7 $\mu g\ C\ l^{-1}$). The PCC concentrations during the blooms of 1995 and 1997 were half the amount observed in 1996, 174.3 $\mu g\ C\ l^{-1}$ and 148.7 $\mu g\ C\ l^{-1}$, respectively. The high PCC in 1996 may again be explained by species composition, specifically by the very high

abundance of the small diatom *Skeletonema costatum*. This small but numerous diatom composed 58% of the PCC for 1996.

There was another anomaly in the PCC when comparing the three years. During the post-bloom of 1997 the average PCC amount was 37.0μg C l^{-1}, nearly twice the amount of the previous two years. This high concentration seen during the post-bloom of 1997 is presumably due to the high abundance of diatoms not observed in 1995 and 1996. The post-bloom phytoplankton communities of those two years consisted of mainly (88-95%) flagellates, but in 1997 the majority of the phytoplankton community consisted of diatom species. During the post-bloom of 1997, 29% of the phytoplankton community was *Chaetoceros* sp., 22% was *Nitzschia* sp., 11% was *Thalassiosira* sp. and 36% was flagellates.

Phytoplankton Cell Carbon to Chlorophyll (PCC:Chl)

The mean PCC:Chl ratios were 14, 20, and 21, respectively for 1995, 1996, and 1997 and all were significantly different from each other. The range of PCC:Chl, from all years, was 7.5 to 31.63.

Although the ratios of PCC to Chl from blooms in the Northern Baltic Sea (19° 48' 07" E, 63° 31' 00" N and 19° 58' 05" E, 62° 35' 00" N) are higher than ratios from this research site, the seasonal trend of ratios were similar (Andersson & Rudehäll, 1993). The highest ratios were observed during the bloom and ratios decreased during the post-bloom and remained low until a small bloom occurred during the recovery.

Since the overall range of PCC:Chl was relatively narrow, there was not a considerable difference in the spring time mean ratios (Table 12.) The mean ratio during

the bloom in 1995 was significantly lower than the mean bloom ratios during this period in the following two years. The PCC:Chl bloom means were 12.9, 23.2, and 20.8, respectively, for 1995, 1996, and 1997. From the post-bloom, the mean PCC:Chl in 1996 (15.0) was slightly higher than the mean in 1995 (13.4) and 1997 (13.6). The highest ratio during the recovery was from 1997 (26.6). The average in 1996 was 14.5 and 1995 was intermediate (18.4)

The PCC:Chl values in this study relate well to ratios estimated in other studies. The ratios observed during the bloom of 1996 and 1997 are slightly lower than ratios (27-67) found in natural populations in Denmark (Riemann et al.1989) but within Taylor et al.'s (1997) predicated ratios for 60°N (20-40). Interestingly, the 1996 and 1997 ratios from this study are similar to the ratios (20-27) for the South Adriatic Sea (Jasprica and Caríc 1997). Ratios as low as those seen in 1995 are described by Booth and Smith (1997) for Greenland's Northeast Water Polyna communities (11-265) and in the coastal waters of the East China Sea (13-94) (Chang et al. 2003).

The mean ratio of PCC that is associated with the chlorophyll, determined from the linear regression of PCC vs. chlorophyll, was 12, 24, and 21, for 1995, 1996, and 1997, respectively. Statistical analysis of the slopes of PCC:Chl suggest that none of the slopes were significantly different from year to year at the $\alpha = 0.05$ significance level. In addition these ratios are similar to the ratios of PCC:Chl described previously in this section (14, 20, 21, respectively, for each year).

Physical and Chemical Effects on C:Chl

This study was completed during years with similar positive values of the Pacific Decadal Oscillation (PDO) (http://jisao.washington.edu/pdo/PDO.latest) in the spring months. An El Niño developed in 1997 but its expression in the Gulf of Alaska was not experienced until late 1997 and spring of 1998 (http://topex-www.jpl.nasa.gov/science/enso97/el_nino_1997.html).

Temperature

Statistical analysis of temperature data indicated no difference in the mean temperature between years. In addition, the range of temperatures for all years was similar as well. A notable interannual difference in the temperature data is the amount of variation in temperature explained by the seasonal progression. For example, in 1995 the linear regression of temperature and Julian Day had a high $r^2 = 0.95$. In 1996 the value decreased to $r^2=0.90$ and dropped more in 1997 to $r^2=0.83$. This decrease in the r^2 value may be explained by the increasing fluctuation in temperature values seen near the end of the sampling seasons of 1996 and 1997.

Linear regression of the PCC:Chl vs. temperature for each year suggests that very little to essentially none of the variance in PCC:Chl can be explained by temperature in any year (1995 $r^2=0.28$, 1996 $r^2=0.08$ and 1997 $r^2=0.00$) (Table 14).

Salinity

Statistical analysis of the salinity data indicated that the average salinities of all three years were significantly different from each other. The average salinity was highest in 1996 (31.38 psu), intermediate in 1997 (31.10 psu) and lowest in 1995 (30.01 psu).The

amount of variance in PCC:Chl that can be explained by salinity was similar to that of the temperature regressions (Table 14). In 1995, 25% of the variance in PCC:Chl can be explained by salinity. Essentially none of the variance in PCC:Chl can be explained by salinity in 1996 and 1997.

Nutrients

Statistical analysis of the nutrient data indicated that only the N+N data were significantly different between years. The average concentration of N+N was highest in 1996 (5.73 μM), intermediate in 1995 (4.76 μM) and lowest in 1997 (3.16 μM).

The N+N concentrations preceding the bloom of 1997 were about half the concentrations of the previous two years. In addition N+N concentrations in 1997 were rarely greater than 5μm suggesting possible N+N limitation (half saturation constant of nitrate for diatoms is 0.4-5.1μm) during the bloom (Valiela 1984). Although not supported by the 1995 and 1996 nutrient plots, the primary producers in Prince William Sound are classically nitrogen limited during summer months (Elsinger et al. 2001, Goering et. al., 1973). The slope of PCC:Chl in 1997 was lower than in 1996 yet higher than 1995 suggesting that nitrogen limitation had no effect on the carbon to chlorophyll ratios. In addition, linear regressions of each nutrient type and PCC:Chl indicate that essentially none of the variance in PCC:Chl can be explained by nutrient concentrations (Table 14).

Interestingly, the nutrient data shows injections of nutrients approximately every 14 days in 1997. As noted by Eslinger et al. (2001), nutrient concentrations increased periodically after the bloom probably due to tidal mixing with deeper waters.

Table 14. Results of linear regressions: PCC:Chl vs physical and chemical variables.

Year	Y	X	r^2
1995	C:Chl	Temperature	0.283
	C:Chl	Salinity	0.254
	C:Chl	N+N	0.139
	C:Chl	PO^4	0.140
	C:Chl	SIO^4	0.038
	C:Chl	Secchi	0.007
1996	C:Chl	Temperature	0.084
	C:Chl	Salinity	0.010
	C:Chl	N+N	0.052
	C:Chl	PO^4	0.014
	C:Chl	SIO^4	0.015
	C:Chl	Secchi	0.411
1997	C:Chl	Temperature	0.000
	C:Chl	Salinity	0.004
	C:Chl	N+N	0.020
	C:Chl	PO^4	0.022
	C:Chl	SIO^4	0.059
	C:Chl	Secchi	0.116

This effect is very apparent in the 1997 data where there are strong pulses of nutrients. This influx of nutrients may be the reason why the diatom community persisted longer in 1997, extending the duration of the bloom in this year.

Water Transparency

The negative slopes from the regressions of secchi depth vs. integrated chlorophyll are similar for all three years and in agreement with the effects of the diatom bloom on light penetration. The more particles in the water column, the less light can penetrate to depth. The r^2 values from the regressions were all above 0.50 suggesting that it is possible to use secchi depth to get a preliminary estimate of chlorophyll. Linear

regressions of PCC:Chl vs. secchi depth suggest that 41% of the variance in PCC:Chl from 1996 can be explained by secchi depth (Table 13). However, only 0.01% and 11% of the variance in PCC:Chl can be explained by secchi depth in 1995 and 1997, respectively.

CONCLUSIONS

- The carbon to chlorophyll ratios, determined by the linear regression of phytoplankton cell carbon to chlorophyll, did not vary significantly between years.
- Changes in phytoplankton species composition explain minor variations in the ratio between years and during the annual progression from the bloom to the recovery.
- Seasonal changes in temperature and salinity accounted for less than 28% of the variance in the ratio during all years studied.
- Nutrient concentrations had no apparent affect on the ratio between years.
- Measurements of parameters used to directly estimate cell carbon lead to the best estimate of the carbon to chlorophyll ratio for the phytoplankton community.
- The particulate organic carbon to chlorophyll ratio is highly variable in this region probably due to varying amounts of non-phytoplankton carbon in the water column. Thus use of this ratio will generally over estimate phytoplankton associated carbon.
- The data from this study indicate a fixed carbon to chlorophyll ratio of 18 is reasonable for estimating carbon associated with phytoplankton in Prince William Sound during the spring bloom in non El Niño years.

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